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**THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS**

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## FIRST DAY.

### WEDNESDAY—AFTERNOON SESSION—*Continued.*

## DRUG SECTION.

### REPORT ON ALKALOIDS.

By A. R. BLISS, JR.<sup>1</sup> (Emory University School of Medicine, Emory University, Ga.), *Associate Referee.*

The work on alkaloids for 1921–1922 included:

#### *I. Assay of Stramonium Ointment.*

The following method was adapted by the associate referee from the assays of *extractum stramonii*<sup>2</sup>, *extractum belladonnae foliorum*<sup>3</sup>, and *fluid-extractum belladonnae radidis*<sup>4</sup> and gave very accurate results.

Introduce 30 grams of ointment of stramonium into a 250 mil centrifuge flask. Then add 150 mils of a mixture of ether, 2 volumes, and chloroform, 1 volume, followed by 10 mils of ammonia water. Shake the mixture vigorously until all fatty matter is dissolved, and then continue to shake for 3 hours on a mechanical shaker. Allow the mixture to stand—the method may be hastened by centrifuging—until complete separation has taken place, and then decant 100 mils of the clear liquid, representing 20 grams of the ointment, into a separator. Extract the alkaloids from the solution in the separator by shaking out repeatedly with weak sulfuric acid until the alkaloids are completely removed. Collect the acid washings in a separator, add ammonia water until the solution is decidedly alkaline to litmus, and completely extract the alkaloids by shaking out repeatedly with chloroform. Evaporate the combined chloroform washings to dryness, dissolve the alkaloids from the residue in exactly 5 mils of 0.1N sulfuric acid and titrate the excess of acid with 0.02N potassium hydroxide, using cochineal as indicator.

Each mil of 0.1N sulfuric acid consumed corresponds to 28.92 milligrams of the alkaloids of stramonium.

The results shown in Table 1 were obtained by the associate referee and M. F. Brown.

Samples of ointment of stramonium were prepared by accurately weighing 3-gram portions of pilular extract of stramonium into 250 mil centrifuge flasks, warming on a water bath until soft, adding 1.7 mils of diluted alcohol and working the alcohol into the extract with a glass rod. Then 7 grams of melted hydrous wool fat were added and thor-

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<sup>1</sup> Presented by A. G. Murray.

<sup>2</sup> U. S. Pharmacopoeia IX, 1916, 161.

<sup>3</sup> *Ibid.*, 144.

<sup>4</sup> *Ibid.*, 178.



oughly mixed, and finally 21 grams of melted benzoinated lard were added to each flask in the same manner. The stirring rods were carefully wiped with pieces of filter paper, and the paper was placed in the proper flasks.

TABLE 1.  
*Results of assay of stramonium ointment by the Bliss method.*

SAMPLE NUMBER	ASSAY OF OINTMENT	ASSAY OF EXTRACT
1	<i>per cent</i> 0.843	<i>per cent</i> 0.832
2	0.829	0.820
3	0.881	0.835
4	0.857	0.829
5	0.849	0.836
6	0.838	0.822
Average . . . . .	0.8495	0.829

Three samples of this carefully prepared ointment of stramonium and three samples of the extract from which it was prepared were sent to six collaborators, but unfortunately (although mailed during the first part of August) only one collaborator reported.

The report on the results of this study will, therefore, have to be postponed.

## II. *Assay of Belladonna Ointment (G. W. Éwe).*

The method, which has been published<sup>1</sup>, was submitted to five collaborators, who were also provided with carefully prepared samples of ointment of belladonna (prepared by the method suggested by Éwe) as well as samples of the extract from which the ointment was prepared. One collaborator only reported.

Éwe's results have been reported<sup>2</sup>.

The following results were obtained by the associate referee and M. F. Brown with samples prepared as above and assayed by the method under study:

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 572.

<sup>2</sup> *Ibid.*, 573.

TABLE 2.  
*Results of assay of belladonna ointment by the Éwe method.*

SAMPLE NUMBER	ASSAY OF OINTMENT	ASSAY OF EXTRACT
1	<i>per cent</i> 1.850	<i>per cent</i> 1.899
2	1.882	1.891
3	1.839	1.876
4	1.877	1.889
Average . . . . .	1.862	1.888

The report of the collaborators' results will have to be postponed.

NOTE.—In both the assay of extract of stramonium and the assay of extract of belladonna leaves, the U. S. Pharmacopœia IX, 1916 methods were used.

#### RECOMMENDATIONS.

It is recommended—

- (1) That the associate referee's method for the separation of quinine and strychnine<sup>1</sup> be adopted as an official method.
- (2) That the method for the assay of physostigma and its preparations, as presented by G. W. Éwe<sup>2</sup>, be adopted as an official method.
- (3) That the method for the assay of fluidextract of hyoscyamus, as suggested by H. C. Fuller<sup>3</sup>, be adopted as an official method.
- (4) That the associate referee's method for the assay of ointment of stramonium (presented in this report) be further studied by collaborators.
- (5) That the method for the assay of belladonna ointment, suggested by G. W. Éwe<sup>4</sup>, be further studied by collaborators.
- (6) That the method for the assay of belladonna liniment, suggested by G. W. Éwe<sup>4</sup>, be submitted to collaborative study.
- (7) That the study of the gravimetric and the volumetric methods for the assay of ipecac and its preparations be continued.
- (8) That methods for the determination of atropine in tablets be studied.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 4: 416; 1922, 5: 567.

<sup>2</sup> *Ibid.*, 1921, 4: 418; 1922, 5: 568.

<sup>3</sup> *Ibid.*, 1922, 5: 569.

<sup>4</sup> *Ibid.*, 572.

## REPORT ON THE SEPARATION OF CINCHONA ALKALOIDS.

By E. O. EATON<sup>1</sup> (Food and Drug Inspection Station, U. S. Appraiser's Stores, San Francisco, Calif.), *Associate Referee*.

Last year's proposed methods<sup>2</sup>, with an additional method for quinine, were sent to several collaborators with samples for analysis.

The samples submitted were of the following composition:

	No. 1	No. 2	No. 3
	<i>gram</i>	<i>gram</i>	<i>per cent</i>
Quinine sulfate (anhydrous).....	0.750	0.375	.....
Cinchonidine sulfate (anhydrous)...	0.375	0.750	.....
Cinchonine sulfate (anhydrous).....	0.375	0.375	.....
Quinidine sulfate (anhydrous).....	.....	.....	100.0

The directions requested the collaborators to add Sample No. 3 to Sample No. 1 or Sample No. 2 and estimate it quantitatively.

The quinidine method is as follows:

*Quinidine Method.*

To 0.3 gram of either Sample No. 1 or Sample No. 2 (or aliquot of solutions) add 0.15 gram of Sample No. 3. Separate Group I by outlined method. Heat the combined washings and filtrate from Group I on the steam bath for 10 minutes. Add 1 gram of potassium iodide, cool, stir to crystallization and place in the ice box for 2 hours, stirring occasionally. Filter the precipitate and wash thoroughly with very dilute acetic acid. Save filtrate and washings for cinchonine determinations, as outlined in method. (A slight precipitate of cream of tartar in the filtrate may come down after the washings have been added, but this may be disregarded.) Dissolve the precipitated quinidine iodide in dilute hydrochloric acid and shake out indicator as outlined in method. Make ammoniacal and extract quinidine with chloroform. Transfer to a dry tared beaker containing a trace of sand, evaporate to dryness, dry at 100°, and weigh. Calculate to anhydrous quinidine sulfate. To check its purity, dissolve in reagent "N"<sup>2</sup> in the proportion of 0.015 gram to each cc., polarize, and calculate the specific rotation.

Reports were received from two analysts. The results and comments of A. G. Murray of the Bureau of Chemistry, Washington, D. C., were of especial interest.

*Collaborative results.*

ANALYST	SAMPLE No. 1		
	Quinine Sulfate- 50 % Present	Cinchonidine Sulfate- 25 % Present	Cinchonine Sulfate- 25 % Present
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A. G. Murray .....	40.2 44.1*	28.9 24.4*	27.6 26.8*
E. O. Eaton .....	44.6	24.1	26.4
C. K. Glycart .....	44.8	27.7	27.1

<sup>1</sup> Presented by E. K. Nelson.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 504.

*Collaborative results—Continued.*

ANALYST	SAMPLE NO. 2			SAMPLE NO. 3
	Quinine Sulfate— 25 % Present	Cinchonidine Sulfate— 50 % Present	Cinchonine Sulfate— 25 % Present	Quinidine Sulfate†
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A. G. Murray.....	21.1 17.9*	48.0 52.5*	26.4 25.7*	..... 98.4
E. O. Eaton.....	23.0	45.3	26.4	98.0
C. K. Glycart.....	18.4 24.1	46.6 47.6	25.7 29.4	..... 101.2

\*Alkaloids precipitated without the use of an indicator.

†Each collaborator mixed a weighed amount of Sample No. 3 with a portion of Sample No. 1 and recovered the quinidine from the mixture.

## COMMENTS.

*A. G. Murray.*—Experiment shows that practically the same results can be obtained without the use of an indicator, as any added acid is at once thrown out of the solution as potassium bi-tartrate, leaving the solution practically neutral. The type of separatory funnel to be used should be left to the discretion of the operator. Smaller quantities of chloroform are sufficient for extraction of the alkaloids. In the formula for determining the percentage of quinine, a minus sign should be used in front of the first term of the numerator. (The specific rotation being negative, a negative sign indicates that the positive value must be used for this term.) The form should read as follows:

$$100 \frac{-[\alpha]_D^{20} - 180}{277.4 - 180} = \text{Per cent of quinine in the total anhydrous alkaloids of Group I.}$$

*C. K. Glycart.*—In my opinion the principle of the method is sound and it should give good results.

## RECOMMENDATION.

It is recommended that the methods be further studied with a view to simplification and greater accuracy.

REPORT ON METHODS OF ANALYSIS OF MORPHINE,  
CODEINE AND DIACETYLMORPHINE (HEROINE).

By C. K. GLYCART (U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.), *Associate Referee on Alkaloids of Opium.*

In accordance with the recommendation approved by the association at the last meeting, the methods of analysis of morphine, codeine and diacetylmorphine were further studied this year.

Three samples, representing commercial tablets, with directions for examination, were sent to the collaborators.

Sample No. 1 contained codeine sulfate with excipient of milk sugar.

Sample No. 2 contained heroine hydrochloride with excipient of milk sugar.

Sample No. 3 contained morphine sulfate with excipient of milk sugar.

The directions for the reagents, the preparation of the samples, and the qualitative tests and quantitative methods were essentially as reported in 1920<sup>1</sup> and adopted as tentative in 1921.

The results shown in the table were obtained by the collaborators—E. O. Eaton, U. S. Food and Drug Inspection Station, San Francisco, Calif.; H. McCausland, The Abbott Laboratories, Chicago, Ill.; William Rabak, U. S. Food and Drug Inspection Station, Minneapolis, Minn., and the associate referee.

*Collaborative results of analysis of samples containing morphine, codeine and diacetylmorphine.*

COLLABORATORS	SAMPLE No. 1	SAMPLE No. 2	SAMPLE No. 3
	Codeine Sulfate	Diacetylmorphine	Morphine Sulfate
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
E. O. Eaton . . . . .	51.90 51.90	9.97 9.92	23.4 23.2
H. McCausland . . . . .	49.61 49.08	9.69 9.72	23.37 23.05
W. Rabak . . . . .	49.05 48.26	9.04 9.10	23.08 22.78
C. K. Glycart. . . . .	50.89 50.63	9.50 9.58	23.07 23.26

## RECOMMENDATION.

It is recommended that the methods of analysis for morphine, codeine and diacetylmorphine be adopted as official.

<sup>1</sup> J. Assoc. Official Agr. Chemists, 1921, 5: 150.

## REPORT ON LAXATIVE AND BITTER TONIC DRUGS.

By H. C. FULLER<sup>1</sup> (Institute of Industrial Research, Washington, D. C.),  
*Associate Referee.*

The work for the year included a further study of the method tested last year for estimating the active ingredients of cascara sagrada, and a study of the method reported last year for assaying aloin.

Samples were sent out to several collaborators who had expressed a desire to engage in the work. The methods used are as follows:

## ASSAY OF CASCARA, RHUBARB AND SENNA.

## GRAVIMETRIC DETERMINATION.

(Use 5 grams of each drug.)

Introduce the sample into an Erlenmeyer flask of 500 cc. capacity; add 200 cc. of chloroform and 50 cc. of 25% sulfuric acid and attach to a reflux condenser (water cooled), using a cork stopper covered with tin-foil. Apply heat of Bunsen flame and allow to boil for 2½ hours. Allow to cool and transfer to a separatory funnel, washing out flask with a little fresh chloroform.

Draw off chloroform solution into another separatory funnel. Add 50 cc. of chloroform to acid mixture, agitate, and after separation has taken place, run chloroform into that previously collected. Repeat procedure. Discard acid mixture.

Collect chloroform shake-outs in an Erlenmeyer or distilling flask, recover about ⅔ of the solvent by distillation and pour the balance into a separator, washing thoroughly to remove final traces of anthraquinones; agitate with 25 cc. of 10% sodium hydroxide; draw off chloroform and subject to another treatment with 10% sodium hydroxide. Draw off chloroform and wash with 25 cc. of water.

Unite alkaline solutions and washing, add excess of hydrochloric acid and shake out three times with chloroform. Discard acid and wash chloroform solution by shaking with 50 cc. of water. Let settle completely, filter chloroform through cotton in stem of funnel into a distilling or Erlenmeyer flask and recover a portion of the solvent. Then pour the balance into a tared dish, washing out distilling flask with chloroform; evaporate solvent; dry at not over 100° for 30 minutes; cool in desiccator and weigh. The weight represents the total anthraquinone bodies in the drug. Preserve the residue for the method which follows:

## COLORIMETRIC DETERMINATION.

Treat the residue of anthraquinone derivatives obtained by the gravimetric assay described with ether until no more color goes into solution, using in all not over 250 cc. Make up to 250 cc. with ether. Each 50 cc. portion then represents 1 gram or 15.6 grains of the drug originally taken.

A portion of the ether extract, which is yellowish red, is poured into a 1½-inch cell of a Lovibond tintometer. The color of this ether solution is matched against the yellow and red slides. Note depth of color and report degrees observed in red and yellow.

Now place 10 cc. of the ether extract, obtained as above described, in a colorimetric tube, such as a Nessler tube; add 10 cc. of strong ammonia and mix thoroughly. Allow to stand 10 minutes, dilute to a total volume of 50 cc., shake again and flick off the

<sup>1</sup> Presented by P. J. Valsear.

ether portion. The red solution is introduced with an  $\frac{1}{8}$ -inch cell of the Lovibond tintometer and matched against the red slides. Note depths of color and report degrees observed.

TABLE 1.  
*Collaborative results on cascara sagrada assay.*

COLLABORATOR	TOTAL ANTHRAQUINONES			
	Gravimetric	COLORIMETRIC		
		Direct	With Ammonia	
	<i>per cent</i>			
W. J. Monran, (Fuller) Institute of Industrial Research, Washington, D. C.	5.84	Yellow 12.0 Red 1.75	Red 6.0	
P. J. Valear, Bureau of Internal Revenue, Washington, D. C.	5.47	Yellow 11.5 Red 0.32	Red 4.5 Yellow 0.54	
J. D. McIntyre, Bureau of Internal Revenue, Washington, D. C.	4.57	Yellow 9.8 Red 0.44	Red 4.25 Yellow 0.54	
H. G. Edmonds, Bureau of Internal Revenue, Washington, D. C.	4.95	Yellow 10.0 Red 0.50	Red 4.52 Yellow 1.0	
C. W. Harrison, U. S. Food and Drug Inspection Station, Baltimore, Md.	4.2* 4.66†	Yellow 16.0 Red 0.00 Yellow 17.0 Red 0.00		
M. M. Woodward, Department of Agriculture, Lansing, Mich.	5.52 5.46	Yellow 9.0 Red 0.26		
C. K. Glycart, U. S. Food and Drug Inspection Station, Transportation Bldg., Chicago, Ill.	2.93 3.10	Yellow 3.60—3.65 Red 0.25—0.25	Red 1.7 ( $\frac{1}{8}$ -in. tube)	
E. S. Rose, W. F. Severa Co., Cedar Rapids, Iowa.	3.24 4.04‡			
Average by method . . . . .	4.52			

\*Extraction continued with sodium hydroxide (3rd paragraph of method) and a further quantity of anthraquinone, 0.52%, obtained.

†Extraction with sodium hydroxide (3rd paragraph of method) and water alternately until no more color was removed. Omitted from average.

‡2 gram sample used Omitted from average.

#### COMMENTS OF COLLABORATORS.

C. W. Harrison believes that the method of extraction as outlined does not result in complete extraction of the anthraquinone bodies. Conducting further work on the method, he carried the extraction to a point where no more color was extracted by the reagents and obtained in this way, 4.66 per cent, as against 4.2 per cent when he followed the method literally.

Regarding the colorimetric procedure, he says:

I had little success, owing to the fact that the shades of color were so different from the standard glasses that comparison was practically impossible \* \* \*. The solu-

tions obtained were really green-yellow and not at all comparable with the yellow or yellow and red mixtures.

*M. M. Woodward.*—I consider that the gravimetric method is very good as it now stands as far as workability is concerned. The tintometer method was not very satisfactory and personally I much prefer the Duboscq colorimeter and a suitable standard such as picramic acid and NaOH.

*C. K. Glycart.*—When the alkaline solution was washed with 25 cc. of water, considerable color was observed to be removed by two washings in addition to the directions given. In the final extraction with chloroform from the acidified aqueous solution, trailing of color was also noticed. This would indicate that all of the emodin is not removed by the number of extractions specified in the method. However, this may be of minor consequence since the bulk of the color was extracted in the first two operations.

Researches conducted during the year, which can not be fully described in this brief report, substantiate, it is believed, the claim that the anthraquinone derivatives are determining factors in the physiological activity of cascara sagrada.

#### ALOIN ASSAY.

The method for the aloin assay was published last year<sup>1</sup>.

TABLE 2.  
*Collaborative results on aloin assay.*

COLLABORATOR	WEIGHT OF DERIVATIVE
	<i>gram</i>
W. J. Monran (Fuller) . . . . .	0.4750
P. J. Valear . . . . .	0.4592
J. D. McIntyre . . . . .	0.4586
R. L. Burritt . . . . .	0.3909
H. G. Edmonds . . . . .	0.4900
E. S. Rose . . . . .	0.4354 (Average of 4 determinations)

Some of the workers outside of Washington reported difficulty with the aloin method, and asked for further details on preparing the reagent. Those who did the work in Washington and were in a position to confer directly with the referee obtained very consistent and concordant results. In sending out the original sheet describing the method, certain typographical errors were overlooked, and it is not unlikely that the ambiguous wording may have led to some confusion.

#### RECOMMENDATION.

It is recommended that the work on the laxative and bitter tonic drugs be continued.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 580.



No report on the determination of calomel, mercuric chloride and mercuric iodide in tablets was made by the associate referee.

## REPORT ON ACETYLSALICYLIC ACID.

By A. E. PAUL (U. S. Food and Drug Inspection Station, Cincinnati, Ohio), *Associate Referee*.

Last year methods for the determination of free and combined salicylic acid and a double titration method for the determination of acetylsalicylic acid were studied and adopted. It was recommended that an effort be made to devise methods for the more difficult determination of free and combined acetic acid, in order that methods for the determination of the two acids which enter into the composition of this product may be available.

There was also submitted, last year, a method for the determination of the melting point, which was referred back to the associate referee for comparison with the method adopted by the association. However, the only methods recognized at this time in the official and tentative methods are intended for use in connection with fats and fatty acids, and are not applicable to aspirin. The method was re-submitted to collaborators this year.

### SAMPLES.

Three samples were submitted. The aspirin was an article of high purity, furnished by Merck and Company. The samples were prepared as follows:

	<i>per cent</i>
"A"—Acetic acid . . . . .	0.25
Acetylsalicylic acid . . . . .	99.75
"B"—Acetylsalicylic acid . . . . .	100.0
"C"—Milk sugar . . . . .	20.0
Acetylsalicylic acid . . . . .	80.0

The readiness with which free acetic acid is dissipated from a powder renders it extremely unlikely that the amount added would correspond at all closely to the amount which would be present at time of analysis. However, an attempt was made to mix the sample thoroughly and place it in the individual containers without undue loss of time.

It is regretted that only four collaborators reported on the work, but it is fortunate that these were all drug analysts of wide experience, and it may be assumed that the results reported represent the practical usefulness of the methods.

Collaborators were requested to examine the samples, using the methods submitted. They were also urged to offer suggestions as to

qualitative or quantitative tests for isomers or closely related substances which might be present, either through faulty manufacture or through intentional sophistication.

It was also pointed out that in the near future it will be necessary to give consideration to methods for determining aspirin in mixtures, and suggestions along this line were solicited.

#### METHODS.

The following methods were submitted:

##### *I.—Melting point.*

If excipients are present, treat 0.2–0.3 gram with small portions of chloroform and filter into a beaker or dish. Evaporate the bulk of the chloroform on the steam bath, and complete by spontaneous evaporation until completely dry. Determine the melting point as directed in the U. S. Pharmacopœia<sup>1</sup>.

##### *II.—Quantitative method for free acetic acid.*

Into a straight calcium chloride tube, 1 inch in diameter, place a loose plug of glass wool, then a layer of fibrous asbestos, then 10 grams of sample, and another layer of asbestos. Pack sufficiently well to hold the layers in place, but not so tight as to prevent the air from passing through freely. Place the tube at an angle of 45°, tapered end down. Pass a slow current of air, free from carbon dioxide and water, downward through the tube for 1 hour and absorb the free acid in 0.02N alkali. Titrate with 0.02N acid, using phenolphthalein as an indicator. (Calculate free acetic acid from the amount of alkali used.)

In case the material to be examined is finely powdered or liable to cake, mix with a suitable amount of coarsely ground asbestos or use alternate layers of material to be examined and asbestos.

##### *III.—Quantitative method for total acetic acid.*

If excipients are present, treat 1 gram with a small portion of chloroform, filter into a beaker and wash until completely extracted. Evaporate the bulk of the chloroform in the steam bath, add 15 cc. of normal sodium hydroxide and evaporate nearly to dryness. If no excipients are present, evaporate 1 gram and the 15 cc. of sodium hydroxide directly in a steam bath nearly to dryness. Transfer into a separatory funnel, using for this operation successively, 10 cc. of water, 10 cc. of dilute sulfuric acid (10% by volume), a small amount of chloroform, and finally an additional 5 cc. of water. Shake successively with 30 cc., 25 cc., 20 cc., 15 cc. and 15 cc. of chloroform. Wash the combined chloroform extractions with 3 portions of water, 3 cc. each. Shake the original aqueous solution with an additional 10 cc. of chloroform, and add this chloroform to the 9 cc. of wash water. Add the chloroform to the main bulk of chloroform.

NOTE.—This chloroform extract contains all the salicylic acid in the sample and may be used for its determination, but ordinarily it is preferable to determine the salicylic acid in a separate portion. Under these conditions the chloroform extracts may be discarded.

Transfer the main bulk of aqueous solution to a 500 cc. flask, rinsing first with the 9 cc. of wash water, and finally rinse both separatory funnels with small portions of water. Steam-distil into 60 cc. of 0.1N alkali, until acetic acid has been distilled over.

<sup>1</sup> U. S. Pharmacopœia, IX, 1916, 596.

This usually requires 500-700 cc. During the distillation keep the bulk in the distillation flask down to 20-25 cc. If the modified Hortvet volatile acid apparatus<sup>1</sup> is available, it is suggested that results obtained by its use be compared with those obtained by the use of an ordinary 500 cc. flask. Titrate the distillate with 0.1N acid, using phenolphthalein as indicator.

NOTE.—It is desirable to add an excess of alkali to the water in the steam generator to avoid presence of carbon dioxide.

The collaborators were the following: E. K. Nelson, Bureau of Chemistry, Washington, D. C.; A. G. Murray, Bureau of Chemistry, Washington, D. C.; C. K. Glycart, Food and Drug Inspection Station, Chicago, Ill.; E. O. Eaton, Food and Drug Inspection Station, San Francisco, Calif.; and C. W. Harrison, Food and Drug Inspection Station, Baltimore, Md.

The results obtained are shown in the table.

*Collaborative results.*

	NELSON	MURRAY	GLYCART	EATON	HARRISON
Sample "A"					
Free acetic acid — 0.25%	0.009	0.025	None	0.029	0.020
Total acetic acid —33.58	36.54	33.5	33.2	25.3	29.2
Melting point	135-137	131-133	131	135.5	135.0
Sample "B"					
Free acetic acid	0.004	0.005	None	None	0.006
Total acetic acid —33.33%	36.39	31.0	31.5	24.8	28.1
Melting point	134-136	133-136	131-133	135.9	135.0
Sample "C"					
Free acetic acid	0.002	0.004	0.008	0.013	0.018
Total acetic acid 26.66%	31.15	27.2	26.7	23.2	23.8
Melting point	135-136	126-130	130.0	133.8	130.0

#### COMMENTS BY COLLABORATORS.

*E. K. Nelson.*—The figures for total acetic acid are above theory. This may be due to the chloroform retained in solution distilling and being saponified by the sodium hydroxide.

*A. G. Murray.*—The use of chloroform should be avoided because of the large amount necessary, and also because of the possibility of its being saponified by the alkali. It might be desirable to substitute 0.2N for 0.1N solutions.

*E. O. Eaton.*—Acetyl acetic acid is rarely found in mixtures, except in prescriptions. The melting point before and after crystallization from chloroform should give an indication of purity. Extended research is hardly necessary. It is unlikely that isomers or closely allied related substances will be found to any extent in the future.

C. W. Harrison made an extremely interesting report, in the course of which he describes briefly a method for total acetic acid devised by himself, based on titration of an aliquot of the acid aqueous liquid before and after boiling off the volatile acid in an open dish. He also

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 167.

suggests that in the method as submitted, it might be preferable to collect the distillate in a receptacle directly, instead of distilling with standard alkali.

#### DISCUSSION OF RESULTS.

The results, while not entirely satisfactory, show that so far as the melting point is concerned, the method yields results which are as close as may be expected from a product which is as unstable as is aspirin. The total acetic acid varies considerably, but it will be noted that at least two of the collaborators obtained almost theoretical figures, which would tend to confirm the experience in this laboratory, that such results are possible of attainment. It is believed, however, that there are inherent difficulties in the details which should be removed before the method is entirely satisfactory.

As to the free acetic acid, it is not believed, as previously stated, that any definite knowledge is available as to the amount actually present at time of analysis. Nevertheless the results are fairly uniform in that they are materially higher for the sample which contains added acid than for the samples which do not.

It is believed, in consideration of all the results, that the method for melting point is satisfactory for tentative adoption, but that the methods for total and free acetic acid should be given further attention with a view to such modification as will result in greater assurance of accuracy and concordance. It is believed that Harrison's suggestion for total acetic acid should be followed and compared with a detailed modification of the method studied this year.

It would also seem desirable to try out Eaton's idea of taking the melting point of the product before and after crystallization from a hot saturated solution as an index of purity.

#### RECOMMENDATIONS.

It is recommended—

(1) That the method for the determination of melting point, as studied last year and again this year, be adopted as a tentative method.

(2) That an attempt be made to amend the details of the method for the determination of total acetic acid, described in this report, and that it be compared with a method based upon the suggestions made by C. W. Harrison.

(3) That the method for free acetic acid be further studied.

(4) That E. O. Eaton's idea of determining the melting point before and after crystallization from hot chloroform be investigated on pure and impure samples.

(5) That the problem of determining aspirin in the presence of possible interfering substances be given consideration.

## REPORT ON METHODS FOR THE DETERMINATION OF PHENOLPHTHALEIN.

By SAMUEL PALKIN (Bureau of Chemistry, Washington, D. C.),  
*Associate Referee.*

The work on phenolphthalein was carried over from the previous year owing to the lack of reports at that time. Two methods of determination and a sample consisting essentially of phenolphthalein and starch were sent to collaborators. The methods were (1) an iodine method, essentially as published by the associate referee<sup>1</sup>; and (2) an ether extraction method submitted by A. W. Hanson, Food and Drug Inspection Station, Chicago.

The methods are as follows:

### *Method I.*

#### OUTLINE.

When a solution containing phenolphthalein and iodine is made, alternately, alkaline to complete solution and acid to complete precipitation, at a low temperature, a quantitative yield of tetraiodophenolphthalein is obtained, which may be extracted by acetone-chloroform mixture and weighed.

#### REAGENTS.

- (a) *Potassium hydroxide*.—100 cc. of 30% solution.
- (aa) *Potassium hydroxide*.—100 cc. of 3% solution.
- (b) *Iodine reagent*.—Dissolve 10 grams of potassium iodide in 60 cc. of water, add 7 grams of iodine and just discharge the free iodine by the addition of (a).
- (c) *Sodium sulfite*.—10 cc. of 15% solution.
- (d) *Acetone-chloroform*.—1 volume acetone to 3 volumes chloroform. (About 160 cc. are required for each determination.)

#### PREPARATION OF SAMPLE.

(1) In the absence of other substances which are themselves, or, on treatment with iodine and alkali, form compounds which are extractable by acetone-chloroform (d) (including most plain phenolphthalein tablets as in Sample No. 1): Count and weigh a suitable number of tablets to ascertain the average weight, grind to a fine powder and mix thoroughly. Treat a weighed amount, corresponding to about 0.5 gram of phenolphthalein, with 12 cc. of potassium hydroxide (aa). When all phenolphthalein has dissolved, transfer to a 50 cc. volumetric flask and make up to volume with water.

(2) In the presence of material extractable by acetone-chloroform (d), particularly chocolate: After the preliminary grinding (or grating) as in (1), weigh out an amount corresponding to about 0.5 gram of phenolphthalein, mix well with an equal amount of sand, and transfer to the thimble of a 100 cc. Soxhlet extraction apparatus. Cover with cotton to prevent loss of floating material and extract with petroleum ether (B. P. 30°–60°) for about 2 hours on a steam bath. Discard the extract, drain the

<sup>1</sup> *J. Ind. Eng. Chem.*, 1920, 12: 766.

thimble, and repeat the extraction with C. P. acetone for 1 hour. Evaporate the acetone extract, including that drained from the thimble, on a steam bath, and dry at 100° to remove all traces of acetone. Dissolve the residue in 12 cc. of potassium hydroxide (aa), transfer to a 50 cc. volumetric flask, and make up to volume.

#### DETERMINATION.

Take an aliquot portion of the solution (filtered if necessary and prepared according to (1) or (2)), sufficient to represent about 0.1 gram of phenolphthalein, usually 10 cc. Run this into a 100 cc. beaker containing 15–20 grams of ice. Add sufficient iodine reagent (b) to insure an excess, the requirement for 0.1 gram of phenolphthalein being about 3.5 cc. Add concentrated hydrochloric acid from a buret drop by drop to complete precipitation. If sufficient iodine has been added, the precipitate, as well as the supernatant liquid, will be brown; if not, add more iodine to insure an excess, and then strong potassium hydroxide solution (a) drop by drop, with stirring to dissolve the precipitate completely and consume all the excess iodine. This solution should be colored blue or blue-purple. Repeat the process of precipitation with strong acid and resolution with strong alkali 3 or 4 times with small amounts of the reagents, adding small pieces of ice if necessary to keep the solution cold. In the acid condition there should be a brown precipitate resembling a periodide, and the supernatant liquid should be colored brown by the excess of iodine. The alkaline solution should be clear blue or purple-blue, and no precipitate should be present. Transfer the alkaline solution with washing to a 150 or 200 cc. separatory funnel and add a small piece of ice. Add 0.5 cc. of 15 per cent solution of sodium sulfite (c) and acidify the mixture with a few cc. of strong hydrochloric acid. Add from 50 to 75 cc. of acetone-chloroform mixture and shake. The tetraiodophenolphthalein precipitate dissolves in the chloroform-acetone. When the layers have separated draw off the chloroform-acetone extract into another separatory funnel, add a few cc. of chloroform-acetone to the first funnel and draw this off also into the second funnel, to effect as complete a transfer as possible. Wash this chloroform-acetone extract with about 20 cc. of water, and when the layers have separated transfer to a weighed Erlenmeyer flask. Make two more extractions using 35 cc. of solvent for each, wash as before and add<sup>1</sup>. Evaporate the total volume of chloroform-acetone extract to dryness on a steam bath, below the boiling point, using air blast if available, taking care to avoid mechanical losses in transfer and evaporation. Dry the residue in an oven at 100°C. for 20 minutes, cool and weigh. The weight of tetraiodophenolphthalein, multiplied by the factor 0.3871, gives the phenolphthalein content.

#### *Method II.*

##### OUTLINE.

Phenolphthalein in the amorphous form, as when precipitated from alkaline solution by acid, may be extracted with ether and determined by weighing the residue.

##### PREPARATION OF SAMPLE.

Ascertain the average weight in the usual manner, and grind to a fine powder.

#### DETERMINATION.

Weigh out a portion representing about 0.1 gram of phenolphthalein, transfer to a separatory funnel by means of 10 cc. of 5% sodium hydroxide solution and a little

<sup>1</sup>NOTE.—If an emulsion is formed in the first extraction, it will be found that on drawing off this emulsion layer into the second funnel there will usually result a further separation into two layers: an upper layer of emulsion and a lower layer of clear chloroform-acetone extract. Draw off this clear lower layer into a third separatory funnel for washing. Pass the subsequent extractions with chloroform-acetone through the second funnel, containing the small amount of emulsion, before washing as indicated above.

water, and extract 3 or 4 times with ether, using 25 cc. for the first and 20 cc. for the following extractions. Run the ether extracts into a separatory funnel and wash twice with 5 cc. of dilute sodium hydroxide solution. (Substances like strychnine, quinine, acetanilid, acetphenetidin, as well as any unsaponified fatty material or mineral oil, if present, will be removed by extraction with ether.) Combine the alkaline solutions and acidify with hydrochloric acid, then extract with ether as before, until all the phenolphthalein has been removed, as determined by testing a portion of the solution with sodium hydroxide. Usually 4 or 5 extractions will be sufficient. Filter the ether extracts into a tared beaker, evaporate, dry the residue at 100°, and weigh. The residue should be soluble in alcohol, showing absence of most oils. When titrated with 0.1N sodium hydroxide, the alcoholic solution should be practically neutral, showing absence of acid extractives, like fatty acids and salicylic or benzoic acid.

*Collaborative results of determinations by the two methods.*

ANALYSTS*	METHOD I	METHOD II	TOTAL ALCOHOL SOLUBLE MATTER
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
O. L. Evenson	71.76	78.3	....
	70.76	78.4	....
	71.69	73.2	....
	.....	77.5	....
	.....	77.4	....
G. C. Spencer†	68.26	70.62	....
	66.35	74.55	....
	69.25	70.33	....
	66.30	70.34	....
	66.90	....	....
	69.53	....	....
	61.73	....	....
	62.02	....	....
	70.6	....	....
	59.7‡	....	....
	59.29‡	....	....
A. G. Murray	69.72	71.6	69.74
C. D. Wright	68.18	....	....
	68.32	72.6	....
	68.38	71.1	....
W. F. Kunke	68.9	71.2	....
	69.5	71.0	....
S. Palkin	69.8	71.8	....
	70.0	73.3	69.9
	69.5	72.5	....

\*Bureau of Chemistry, Washington, D. C.

†Applied Method I to a stock sample of phenolphthalein and obtained 98.0% recovery.

‡Stood 24 hours in alkaline solution.

The following additional memorandum was sent out later:

*Method I.*

One of the collaborators has found the following modification in the preparation of the sample of advantage in preventing gelatinization of starch. He says:

Thoroughly wet the powder with 12 cc. of water, add 12 cc. of 3% potassium hydroxide, transfer to a 50 cc. flask and make up the volume. I found it advantageous to reserve a portion of the alkali for the washings. In this way it was easily possible to determine when the phenolphthalein had been completely dissolved and transferred. This solution filtered through paper with the greatest ease and occasioned no difficulty subsequently either in the precipitation or the extraction.

*Method II.*

Another collaborator states that he at first neglected to filter the ether extract of phenolphthalein and found his results much higher than when filtering as directed in the method. Attention is called to the necessity of filtering.

COMMENTS AND RECOMMENDATIONS.

With the exception of those obtained by Spencer, the results with Method I were fairly concordant—as nearly so as could be expected in the hands of different analysts. The tendency was to get somewhat low results by this method. With the exception of Evenson and Spencer (one determination) the collaborators also obtained fairly concordant results with Method II, but the tendency here was to get high results.

In view of the inconsistencies shown in the results of these two collaborators, the associate referee does not recommend the tentative adoption of these methods at the present time. It is suggested that further study be made to determine possible sources of error, and that such changes and simplifications be incorporated as will render the methods more certain in the hands of different collaborators.

REPORT ON QUALITATIVE AND QUANTITATIVE METHODS  
FOR THE EXAMINATION OF PROCAINE (NOVOCAINE).

By ALFRED W. HANSON (U. S. Food and Drug Inspection Station,  
Transportation Building, Chicago, Ill.), *Associate Referee.*

The methods submitted last year for the examination of procaine (novocaine) were studied further, as well as the extraction and titration of the procaine base from an ammoniacal solution. Samples were sent to collaborators and the results have been tabulated.

Procaine is sometimes used in the form of procaine nitrate as it can then be administered with silver nitrate. A study was made of the effect of nitrates on the bromide-bromate titration, and it was found that small amounts of nitrates do not interfere with this titration.



## DESCRIPTION OF SAMPLES.

No. 1.—Consisted of commercial procaine hydrochloride.

No. 2.—Contained 50 per cent of commercial procaine, balance sodium chloride.

No. 3.—Contained 17.8 per cent of commercial procaine, balance sodium chloride.

No. 4.—Contained 11.77 per cent of commercial procaine, 44.2 per cent of potassium nitrate and 44.1 per cent of sodium chloride.

The procaine used in the mixtures was the same as Sample No. 1.

The qualitative tests, bromide-bromate method and extraction method were essentially the same as submitted to collaborators the past two years<sup>1</sup>.

The following results of the determinations by the different methods, on varying samples, were obtained by the associate referee; H. McCausland, 4753 Ravenswood Ave., Chicago, Ill.; and J. H. Bornmann, 1625 Transportation Bldg., Chicago, Ill., collaborators:

*Collaborative results on the determination of procaine.*

BROMINATION METHOD				
COLLABORATOR	SAMPLE No. 1 100% PROCAINE	SAMPLE No. 2 50% PROCAINE	SAMPLE No. 3 17.8% PROCAINE	SAMPLE No. 4 11.77% PROCAINE
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
H. McCausland.....	99.0	50.18	17.54	11.93
	98.9	52.65	17.58	11.52
	98.7	50.52	.....	.....
		51.53	.....	.....
A. W. Hanson.....	99.6	50.2	17.7	11.8
	98.3	49.5	17.4	11.7
J. H. Bornmann....	100.1	48.91	17.02	11.49
	99.2	49.14	17.11	11.44
Average.....	99.1	50.3	17.4	11.6

EXTRACTION METHOD				
H. McCausland.....	99.5	52.89	17.45	11.43
	99.23	51.67	17.56	11.44
A. W. Hanson.....	98.1	49.9	16.7	11.2
	98.2	49.6	16.9	11.4
J. H. Bornmann....	97.75	47.08	16.13	11.17
	97.20	46.79	16.24	11.17
Average.....	98.3	49.6	16.8	11.3

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 163; 1922, 5: 589.

## COMMENTS ON THE QUALITATIVE TESTS.

*J. H. Bornmann:*

*Test No. 1.*—Under the conditions of this test a brown precipitate is formed in the cold, accompanied by a strong odor of acetaldehyde. Cocaine shows no reduction of the permanganate and there is no aldehyde odor noticeable.

*Test No. 2.*—Mayer's reagent causes the formation of a white precipitate which is soluble in dilute sulfuric acid. Cocaine and stovaine also yield white precipitates under the same conditions; however, they are not soluble in dilute sulfuric acid.

*Test No. 3.*—Procaine is readily hydrolyzed when treated as indicated in this test and no precipitate is formed with Mayer's reagent on the residue from the chloroform extract of the hydrolyzed sample. Stovaine is not hydrolyzed when treated in the same way as is shown by the fact that the chloroform residue gives a white precipitate with Mayer's reagent.

**NOTE BY REFEREE.**—In testing the extracted residue with Mayer's reagent, about 1 cc. of 0.1N sulfuric acid should be added so as to bring the oily base into solution in case stovaine is present.

*Test No. 4.*—Under the conditions of this test procaine yields a dark red solution and a red precipitate. Cocaine gives a yellow precipitate which dissolves to a yellow solution while stovaine gives a bright yellow precipitate.

*Test No. 5.*—Procaine reduces potassium permanganate at once when treated by this test, leaving a port-wine-colored solution. Cocaine does not respond to this test.

*Test No. 6.*—When a small amount of pure procaine is treated with 1 cc. of concentrated sulfuric acid there is no visible darkening. This shows the absence of impurities which would be charred by concentrated sulfuric acid.

## COMMENTS ON QUANTITATIVE METHODS.

*H. McCausland.*—In case of Method 2, I prefer to titrate the residue directly with 0.02N acid, omitting the back titration with 0.02N alkali.

*J. H. Bornmann.*—Of the two quantitative methods used, the bromination method is preferable except in cases where it is necessary to extract the procaine with chloroform. In this case it is simpler to titrate with standard acid.

Uniformly higher results were obtained with the bromination method. This method involves the use of more reagents and requires more time than simple titration with acid, but it is easier of manipulation than acid titration unless it is necessary to extract with chloroform.

It should be borne in mind that it is necessary to use the utmost care to prevent loss when extracting the procaine in the case of pure samples, for with a portion of only 0.1 gram taken for analysis any error or loss is multiplied a thousand-fold.

## DISCUSSION.

The results obtained by the different methods this year as well as last year show that the bromide-bromate method is the more accurate. The bromide-bromate method is especially useful in indicating whether

all the substance being assayed is procaine. In cases where it is necessary to extract the procaine base the residue can be converted into procaine hydrochloride in the manner described in last year's report<sup>1</sup>. The acid and alkali titration method (Method 2) should only be used when it is known that the residue after extraction consists of the pure procaine base, in which case it is also a satisfactory method. The procaine base being oily it is a little more difficult to titrate with acid than the ordinary alkaloids, as it does not dissolve so readily. Solution of the procaine base may be facilitated by the addition of 1-2 cc. of neutral alcohol. The addition of a large amount of alcohol is not desirable as the end-point with methyl red indicator is not so sharp.

#### RECOMMENDATIONS.

It is recommended—

(1) That the qualitative tests and the bromide-bromate quantitative method presented at the last two meetings of the association be adopted as the official method for the determination of procaine.

(2) That the extraction and titration method for the quantitative determination of procaine submitted at the last meeting of the association be adopted as the official method for the determination of procaine.

#### REPORT ON METHODS FOR THE EXAMINATION OF MEDICINAL METHYLENE BLUE.

By HARRY O. MORAW<sup>2</sup> (U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.), *Associate Referee*.

No method for the estimation of methylene blue has been adopted by this association. There is no assay in the U. S. Pharmacopœia for it. In color laboratories the reduction method with titanium trichloride<sup>3</sup> is generally accepted as satisfactory for estimating methylene blue as well as other reducible dyes. This method, however, is not considered practicable for the average laboratory<sup>4</sup>.

The literature on methods for drug analysis does not contain a specific and effective method for separating or estimating methylene blue. The Pharmacopœial tests are useful mainly for distinguishing the technical from the medicinal product, by indicating a limit of impurities.

In drug analysis, because of its intense blue color, methylene blue frequently interferes with qualitative tests for other ingredients, and its estimation is generally not undertaken. Since it is frequently dis-

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 591.

<sup>2</sup> Presented by C. K. Glycart.

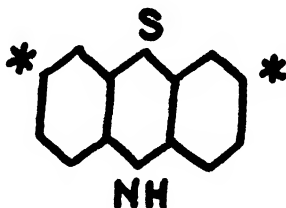
<sup>3</sup> *J. Soc. Dyers and Colourists*, 1906, 21: 9.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1904, 23: 1047.

pensed in capsules, pills or tablets, both alone and mixed with a variety of other ingredients where the quantity of methylene blue is declared, a method of separating and estimating it should be available.

#### PREPARATION AND USES.

Methylene blue is a synthetic dye color belonging to the class of thiazines, or dyestuffs which are derived from a parent substance, thiodiphenylamine<sup>1</sup>, in which two benzene nuclei are united by a nitrogen and a sulfur atom. The leuco base may be obtained from the diamino-

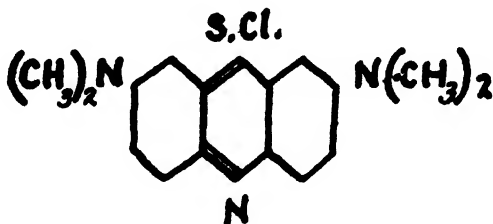


thiodiphenylamine on oxidation. This is further oxidized to methylene blue<sup>2</sup>. It may also be made by reduction of an acid solution of nitro-sodimethylaniline with hydrogen sulfide or zinc dust, then oxidation with ferric chloride in the presence of hydrogen sulfide<sup>3</sup>. Both the hydrochloride of the base and the zinc chloride double salt—

$C_{16}H_{18}N_3S \cdot Cl \cdot 3H_2O$  = the hydrochloride (medicinal)

$(C_{16}H_{18}N_3S \cdot Cl_2 + ZnCl_2) + H_2O$  = zinc chloride double salt (technical)—

are known as methylene blue. It is only the former that is used in medicine, where it is known as the U. S. P. product, or tetramethylthionine chloride<sup>4</sup>.



From the samples received in this laboratory and from standard references on drugs it has been learned that methylene blue is dispensed in capsules, pills and tablets, and is found by itself and in mixtures with

<sup>1</sup> Allen's Commercial Organic Analysis, 4th ed., vol. 5, 353.

<sup>2</sup> Schultz and Julius. Organic Coloring Matters, 1908, 248.

<sup>3</sup> Allen's Commercial Organic Analysis, 4th ed., vol. 5, 354; Cohen's Organic Chemistry, 1907, 408.

<sup>4</sup> Allen's Commercial Organic Analysis, 4th ed., vol. 5, 354.

copaiba, ground nutmeg, kava-kava extract, methyl salicylate, santalwood and cinnamon oils, and a few other ingredients which are commonly used as gonorrhea remedies. As a kidney remedy it may be found with buchu, juniper, potassium nitrate or acetate, copaiba, cubeb, and methyl salicylate, as well as aloes and other plant extractives. Recent research work at the University of Chicago with this compound was reported to have shown that methylene blue destroys tuberculosis germs.

#### METHODS CONSIDERED.

By reference to its formula, it will be seen that the molecule of methylene blue contains, besides carbon, hydrogen and water of hydration, three atoms of nitrogen and one each of chlorine and sulfur.

#### *Loss on drying methylene blue.*

	<i>per cent</i>
Water in $C_{16}H_{18}N_3ClS \cdot 3H_2O$ .....	14.448
Loss over sulfuric acid (several days) .....	12.20
Loss at 98°C.....	13.60
Loss at 103°C.....	14.30

Attempts to develop a gravimetric method were based upon the following:

- (a) Determination of sulfur content after fusion.
- (b) Weighing the precipitate formed with potassium perchlorate<sup>1</sup>.
- (c) Weighing the precipitate formed with potassium iodide or dichromate<sup>2</sup>.

Results with (a) were unsatisfactory because complete fusion was extremely difficult. The precipitates formed in (b) and (c) began to dissolve immediately on washing.

Attempts to develop a volumetric method were based upon the following:

- (d) Adding excess of potassium iodide, or potassium dichromate, filtering out the precipitate and titrating the excess of the precipitant.
- (e) Adding excess of iodine in potassium iodide and titrating the excess of the precipitant.

Results with the potassium iodide were unsatisfactory because the chlorine of the methylene blue interfered with the titration. The excess iodide may be estimated as thallous iodide if the thallium sulfate reagent is available. Results with standard iodine solution were satisfactory.

<sup>1</sup> Attack, F. W. J. Soc. Dyers and Colourists, 1913, 29: 9.

<sup>2</sup> Allen's Commercial Organic Analysis, 4th ed., vol. 5: 354.

The reduction method was given a few trials using stannous chloride. Titanium trichloride, which is generally better, was not available. This method appears to give results equally as satisfactory as the proposed iodine method, but the precautions required to conduct titrations in a current of carbon dioxide and preserve the standard solution out of contact with air to prevent oxidation are as objectionable as methods requiring such precautions usually are.

#### PRINCIPLES OF THE PROPOSED METHOD.

The proposed method is based upon experiments suggested by methods on the use of methylene blue in iodine titrations instead of starch, by Sinnatt<sup>1</sup>. With iodine in potassium iodide solution, methylene blue forms a brown precipitate which was found to be more stable than the purple-violet precipitate formed with potassium iodide alone, and described by Allen as the mono-iodide  $C_{16}H_{18}N_3SI$ . The solubility of the brown precipitate was such that it would not lend itself to washing and making a gravimetric determination. Efforts were then directed toward estimating the methylene blue by addition of excess iodine and titrating the excess with thiosulfate. Great difficulty was experienced in completing the reaction.

While working along these lines it was noticed by C. K. Glycart, U. S. Food and Drug Laboratory, Chicago, that the reaction was more satisfactory if the standard iodine solution was added very slowly until the blue coloration disappeared. At his suggestion also, a larger sample was used for the determination and found more satisfactory. It was necessary to use some further means of stabilizing the reaction, *i. e.*, to cause as much iodine to react with the molecule of methylene blue as possible. Varying amounts of sodium bicarbonate or sulfuric or hydrochloric acid did not give satisfactory results, but the addition of glacial acetic acid in excess gave such promise that a large number of determinations were conducted to ascertain the concentration of sample, acid and iodine, and the time required for the reaction to take place. It was concluded from the results that in the presence of excess iodine and glacial acetic acid the amount of sample could vary 50 milligrams without greatly affecting the results. This reaction takes place as though the molecule of methylene blue absorbs five atoms of iodine, which would make 1 cc. of 0.1N iodine equivalent to 0.007475 gram of methylene blue. Fortunately, acetic acid is particularly adapted as a solvent for this dye. It will remove traces of it from the sides of beakers where even hot water and alcohol are ineffective.

The samples of methylene blue used in this work were the medicinal product furnished by different manufacturers. Their purity was ap-

<sup>1</sup> *Analyst*, 1910, 35: 309.

proximately verified by determining the water of hydration and calculating back to the theoretical the results obtained by the method described in this report. Some of the results showing the variation in loss on drying are shown in Table 1. They indicate that the loss is principally water of hydration and that the samples used were of high purity.

#### SEPARATION OF METHYLENE BLUE.

Methylene blue is almost insoluble in chloroform, ether, carbon tetrachloride, or ethyl acetate and is not extracted to an appreciable extent from acid or alkaline solutions with these solvents. Amyl alcohol is the only common solvent which extracts it satisfactorily. This may be done from a 5-6 per cent salt solution and the dye then removed from the amyl alcohol by diluting the latter with gasoline and shaking out the dye with water<sup>1</sup>. Methylene blue, however, is more readily soluble in dichlorhydrin which, although a less common solvent, is more convenient when there is occasion to use carbon tetrachloride in conjunction with it. The effect of dichlorhydrin in extracting methylene blue was recently noted by A. W. Hanson, U. S. Food and Drug Laboratory, Chicago. The principles employed in the proposed method for the extraction of methylene blue and its removal from the solvent by dilution with carbon tetrachloride are substantially the same as used by Mathewson<sup>1</sup>. Nothing new is claimed for the method of separation, but it is obvious that with the alternate use of carbon tetrachloride or petroleic ether and dichlorhydrin or the other solvents referred to above, a suitable separation could be made of a product containing vegetable oils, methylene blue and plant extractives, thus saving time and making a more effective analysis.

TABLE 1.  
*Results of examination of methylene blue samples.*

SAMPLE NO.	LOSS ON DRYING	WEIGHT OF SAMPLE	METHYLENE BLUE FOUND		ASH
	<i>per cent</i>	<i>mgs.</i>	<i>mgs.</i>	<i>per cent</i>	<i>per cent</i>
96	15.1	120	116.4	97.0 98.2*	0.72
97	11.6	120	122.88	102.4 99.5*	1.1
98	11.6	120	122.88	102.4 99.5*	1.1

\*Calculated to theoretical water of hydration in sample taken.

#### METHYLENE BLUE ASSAY.

The following are the reagents required, instructions for preparation of sample and details of the method of separation and estimation:

<sup>1</sup> U. S. Dept. Agr. Bull. 448.

## REAGENTS.

(1) For separation from oils and soluble and insoluble material:

- (a) *Dichlorhydrin.*
- (b) *Carbon tetrachloride.*
- (c) *Glacial acetic acid.*

(2) For the estimation:

- (a) *0.2N iodine in potassium iodide.*
- (b) *0.1N sodium thiosulfate.*
- (c) *Glacial acetic acid.*
- (d) *Starch indicator.*

## PREPARATION OF SAMPLE AND DETERMINATION OF WEIGHT OF INDIVIDUAL TABLETS OR NET WEIGHT OF CAPSULES.

1.—*Tablets or medicinal methylene blue.*

Weigh separately at least 20 tablets to ascertain the variation in weight. Weigh collectively all unbroken tablets and calculate the average weight per tablet. Powder finely in a mortar at least 10 tablets or 5 grams of methylene blue and protect from moisture in a weighing bottle.

2.—*Capsules.*

Count and weigh a representative number of capsules, and ascertain the gross weight per capsule. Open and transfer as much as possible of the contents to a weighing bottle. Deduct the weight of the cleaned, empty capsules from the gross weight and calculate the average net contents. To clean the gelatine capsules cut in two if necessary and wash by agitating with alternate portions of alcohol and ether. Repeat until thoroughly clean, finally removing the ether before a fan or air blast. A few drops of glacial acetic acid mixed with the alcohol aids in the cleaning.

## METHODS.

NOTE.—When the sample is considered to be pure methylene blue, omit Paragraphs 1 and 2 below and begin in 3 with "weigh accurately into a 50 cc. beaker". If mixed with water-soluble materials only, start with Paragraph 2. If mixed with water-insoluble materials or oils, start with Paragraph 1.

1.—*Separation of Methylene Blue from Oils or Insoluble Material.*

Transfer to a 150 cc. beaker, an accurately weighed amount of the sample prepared as above, corresponding to 100-140 mgs. of methylene blue. Add 15 cc. of carbon tetrachloride, and stir with a glass rod to dissolve the oils while warming on the steam bath a few minutes. Remove from bath and add 15 cc. of hot water while stirring. Warm and stir again a few minutes. Transfer to a 100 cc. separatory funnel, using not more than 50 cc. of hot water and a little carbon tetrachloride if necessary. Cool under tap, shake to extract oils and allow to settle. Turn funnel upside down gently to aid settling. (The line of separation may not be discernible until nearly all the carbon tetrachloride is drawn off.) Draw the carbon tetrachloride into a similar funnel for further treatment with all the undissolved material. A clear aqueous solution of the blue should now remain in the first funnel. If not clear, extract with another 15 cc. portion of carbon tetrachloride, which is added to that in the second funnel, removing if possible any insoluble material with it. If this second extraction is not made add about 10 cc. of fresh carbon tetrachloride to the second funnel, and begin removing with water the methylene blue now in the second funnel by shaking vigorously with 20 to 40 cc. portions of water until practically no more blue is extracted by the water. A few drops of glacial acetic acid hastens this extraction. Combine these



aqueous extracts in a 400 cc. beaker with the main solution from the first separatory funnel, cover with an inverted watch glass on glass rods, and evaporate by boiling gently on a wire gauze. If the total volume of these extracts exceeds 300 cc., use a second 400 cc. beaker for the last extractions and combine the two solutions after evaporating to a total volume of about 50 cc. Now proceed under Paragraph 2, below. Reserve the carbon-tetrachloride solution for qualitative tests for oils if necessary.

## 2.—Separation of Methylene Blue from Water-soluble Materials.

If the sample is entirely soluble in water and contains other ingredients, it will be necessary to extract with dichlorhydrin. Use either the aqueous solution from Paragraph 1, above, or an accurately weighed portion of the sample, corresponding to 100–140 mgs. of methylene blue. Dissolve completely by heating on the steam bath in a 150 cc. beaker with about 50 cc. of water for half an hour, shaking occasionally. Transfer to a 100 cc. separatory funnel, keeping the volume as small as possible. Extract with dichlorhydrin, using 12, 5, 3, and 2 cc. portions. The volume of this solvent must be kept down because it is later diluted with 3 or 4 volumes of carbon tetrachloride. If more or less than 12 cc. will start the first separation it may be tried. This solvent settles very slowly. Rotating the funnel while adding a few cc. of water or spinning the funnel every few minutes hastens it, but each extraction should be allowed to stand until the settling is as complete as possible before making another extraction. The aqueous solution should finally appear almost free from color.

Combine the dichlorhydrin extracts in a 200–300 cc. separatory funnel, add 3 or 4 times their volume of carbon tetrachloride and extract the dye with water by repeated vigorous shaking with 30–50 cc. portions. A few drops of glacial acetic acid hastens the removal. From the combined aqueous extracts remove any traces of dichlorhydrin by shaking out once with about 15 cc. of carbon tetrachloride, which is drawn off after settling about 5 or 10 minutes. Evaporate the aqueous extracts to about 50 cc. over a flame, covering the beaker as before with an inverted watch glass; transfer to a 200 cc. volumetric flask and proceed as under the determination, Paragraph 3.

## 3.—The Determination.

Use either the aqueous solution from Paragraph 2, or weigh accurately into a 50 cc. beaker 100–140 mgs. of the finely powdered sample. Transfer to a 200 cc. volumetric flask, using sufficient water so that the total volume shall equal approximately 1 cc. of water for each milligram of methylene blue. Dissolve completely by heating on the steam bath with frequent shaking during one-half hour. (It is necessary to conduct a blank in the same manner as the determination except the water and acetic acid need not stand before adding the iodine.) Cool; with graduate add 30 cc. of glacial acetic acid; shake thoroughly and allow to stand at least 25 minutes. Add from a buret a total of 30 cc. of 0.2N iodine, adding the first 10 cc. by fast drops with constant rotating of the flask, and the remaining 20 cc. full speed. Stopper flask and allow to stand 50 minutes, shaking thoroughly 5 or 6 times during the interval. Make up to mark with water, shake and let stand 10 minutes longer. Filter rapidly through dry, folded, 12 cm. filter paper. Titrate 100 cc. aliquot with 0.1N thiosulfate with or without starch indicator, according to whether it is a dark or sunny day. Subtract the cc. of thiosulfate from the cc. used to titrate a blank run in same way.

1 cc. 0.1N iodine = 0.007475 gram methylene blue U. S. P.

$C_{15}H_{13}N_2ClS \cdot 3H_2O = 373.75$

Water of hydration in  
methylene blue  $= \frac{54}{373.75} \times 100 = 14.448\%$ .  
U. S. P.

## METHYLENE BLUE SAMPLES FOR COLLABORATIVE WORK.

It has been found that the water of hydration in medicinal methylene blue varies in different samples. This method has not been tried on technical methylene blue.

Sample No. 1 is medicinal methylene blue, U. S. P., approximately 100 per cent. Sample No. 2 is a mixture of methylene blue and milk sugar, 50 per cent of each, which is intended to compare with coated tablets of methylene blue. Use about 250 milligrams for determination. Sample No. 3 is a mixture representing the more or less recognized formula for methylene blue compound. This sample contains approximately 20 per cent of methylene blue U. S. P. mixed with milk sugar, magnesium carbonate, ground nutmeg and oils of sandal, copaiba and cubebs. Use about 600 to 700 milligrams for determination.

The qualitative tests for the other ingredients in the mixtures need not be made in these samples.

TABLE 2.

*Collaborative results on iodine method for determination of methylene blue.*

COLLABORATOR	SAMPLE No. 1— 100 %	SAMPLE No. 2— 50 %	SAMPLE No. 3— APPROXIMATELY 20 %
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
C. F. Jablonski, U. S. Food & Drug Laboratory, New York.....	100.12 100.15	49.95 50.09	20.33 Lost
H. O. Moraw.....	100.4 100.7	49.87 49.03	20.78 20.78 20.98 21.01
A. L. Burns, U. S. Food and Drug Laboratory, St. Louis.....	101.0 102.7	48.25 54.91	20.48 21.18
H. C. Fuller, Industrial Research Institute, Washington, D. C.....	99.85	50.4	20.5
H. Wales, Bureau of Chemistry, Washington, D. C.....	See note on method with	comparison of with $TiCl_3$ method.	iodine method.

## SUGGESTIONS BY COLLABORATORS AND OTHER ANALYSTS.

*C. K. Glycart.*—The plan of adding the iodine to the methylene blue slowly to produce complete precipitation is due to an observation while running a determination during the development of the method.

*A. W. Hanson.*—For the determination of the average weight per tablet, the weight of the loose powder in bottles should be considered as having been rubbed loose from tablets after leaving the factory.

*C. F. Jablonski.*—Use larger amounts of dichlorhydrin (as 25, 20 and 10 cc. portions) in extracting the color because considerable insoluble material other than the color

oxidizable in iodine (starches, leuco base, etc.) will otherwise be carried down mechanically. Experienced difficulty separating methylene blue from gelatine capsules because the color permeates the capsule. Prefer using petrolic ether to remove the oils instead of carbon tetrachloride. It may interest you to know that by using titanium trichloride for titration as per the method outlined below I obtained the following figures:

	<i>per cent</i>
Sample No. 1.....	99.57
Sample No. 2.....	49.80
Sample No. 3.....	20.52

Another sample of methylene blue obtained in our laboratory gave the following results:

	<i>per cent</i>
By iodine method.....	82.22
By titanium trichloride.....	82.08

Thus very good checks were obtained by these two methods. The iodine method may be more accurate but the titanium trichloride method is much speedier and does not require nearly so many separations with solvents. The following is an outline of the method:

*Titanium trichloride method (Jablonski).*

Place 15-30 capsules in a 500 cc. volumetric flask, add about 200 cc. of cold water and let stand until the gelatin is disintegrated (usually 4-5 hours). Heat on the steam bath until all soluble material is dissolved. After cooling, add 20 cc. of glacial acetic acid and make the solution up to the mark with water. After thorough mixing, pipet a convenient aliquot (50 cc.) into a separatory flask and extract with an equal volume of petrolic ether. Filter the water layer into a 200 cc. Jena flask, wash the petrolic ether layer twice with 20 cc. of acetic acid (1 to 10) and pass the washings through the filter. After the addition of about 10 grams of sodium acid tartrate, heat the combined filtrates to boiling and titrate hot with 0.1N titanium trichloride in a current of carbon dioxide.

1 cc. of 0.1N titanium trichloride = 0.018688 gram of  
methylene blue as  $C_{16}H_{18}N_2ClS_3H_2O$ .

Very good results are obtainable if the end-point is watched carefully in going from blue to brown.

*A. L. Burns.*—The titanium trichloride method should be considered, but for the average laboratory the iodine method is perhaps very much better because it is not very practicable to make up 0.1N solution of titanium trichloride.

*H. Wales.*—It was impossible to extract the methylene blue with the amount of dichlorhydrin suggested. About twice the amount should be used. The volume need not be measured accurately. It is believed that the U. S. Pharmacopoeia is wrong in giving methylene blue with three molecules of water. The authorities for this disagree, and their work is not reliable. In all cases of color work the dye present should be computed as anhydrous whether it has the property of forming hydrates or not and, if desired, the allowable percentage of water given. The following figures were obtained on the samples submitted. For your convenience the per cent dye as obtained from the iodine method in Sample No. 1 has been recomputed assuming 3  $H_2O$ . Sample No. 1. analyzed 14.19% water.

SAMPLE NO.	TITANIUM TRICHLORIDE TITRATION	IODINE METHOD	SPECTROPHOTOMETER	DYE AS 3 H <sub>2</sub> O IODINE METHOD
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	86.43	87.23	86.5	101.04
2	43.35	41.84	42.8	48.93*
3	18.04	16.65	17.7	19.46*

\*Calculated to 3 H<sub>2</sub>O by Moraw.

The titanium trichloride method is preferable when available. It was found that the size of the filter paper used for the final filtration seriously affected the iodine value obtained. In view of this it would seem advisable to filter through glass wool or asbestos.

#### RECOMMENDATION.

It is recommended that the iodine method for the determination of methylene blue be adopted by the association as a tentative method, and that further collaborative work be done on the method during the year 1923.

#### REPORT ON QUALITATIVE AND QUANTITATIVE METHODS FOR THE DETERMINATION OF PYRAMIDON.

By ALFRED W. HANSON (U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.), *Associate Referee*.

As pyramidon is one of the newer synthetic preparations that have attained a wide use at the present time, it was thought advisable to study the existing qualitative and quantitative methods for the detection and determination of this substance and, if necessary, develop new methods.

Pyramidon—dimethylaminoantipyrine—differs from antipyrine in having a hydrogen atom of the pyrazolon nucleus replaced by the dimethylamino group. It occurs as small, colorless, almost tasteless crystals which melt at 108°C. It is soluble in 20 parts of water, readily soluble in alcohol, but less readily soluble in ether. As antipyrine is a very closely related substance, it is also desirable to have tests which will detect antipyrine in the presence of pyramidon and pyramidon in the presence of antipyrine.

#### QUALITATIVE METHODS.

##### REAGENTS.

(a) *Ferric chloride*.—Dissolve 10 grams of ferric chloride in 100 cc. of distilled water.

(b) *Iodine reagent (Wagner's reagent)*.—Dissolve 2 grams of iodine and 6 grams of potassium iodide in 100 cc. of distilled water.

(c) *Mercuric potassium iodide solution (Mayer's reagent).*—Dissolve 1.3 grams of mercuric chloride in 60 cc. of water. Add 5 grams of potassium iodide dissolved in 10 cc. of water and make up to 100 cc. with water.

(d) *Silver nitrate solution.*—Dissolve 5 grams in 100 cc. of water.

(e) *Sodium nitrite.*—Dissolve 0.2 gram in 100 cc. of water.

### QUALITATIVE TESTS.

(1) Dissolve 0.01 gram of pyrimidon in 2 cc. of water. Add a few drops of yellow concentrated nitric acid (containing nitrous acid). Pyrimidon gives a purplish blue color.

(2) Dissolve 0.01 gram of pyrimidon in 2 cc. of water. Add a few drops of mercuric potassium iodide solution (c). The solution remains clear. Acidify with a few drops of 10% sulfuric acid. A heavy, light yellow precipitate is formed.

(3) Dissolve 0.01 gram of pyrimidon in 2 cc. of water. Add a few drops of iodine reagent (b). A reddish brown precipitate is formed which does not dissolve on addition of 10% sulfuric acid.

(4) Dissolve 0.01 gram of pyrimidon in 2 cc. of water. Add 1 cc. of ferric chloride solution (a). Pyrimidon, if present, gives a purple to violet color which becomes red on the addition of 10% sulfuric acid.

(5) Dissolve 0.1 gram of pyrimidon in 2 cc. of water. Add a few drops of silver nitrate solution (d). After a few seconds a purple to violet coloration is produced and a deposit of metallic silver is formed on standing.

NOTE.—This test is useful in detecting pyrimidon in antipyrine.

(6) Dissolve 0.01 to 0.02 gram of pyrimidon in 2 cc. of water. Add 1 or 2 drops of dilute sodium nitrite solution (e) and a few drops of 10% sulfuric acid. Shake for a few seconds. A purplish blue coloration is slowly produced which gradually disappears, leaving a colorless solution. A large excess of sodium nitrite should not be added as it destroys the color.

NOTE.—This test is useful in detecting antipyrine in the presence of pyrimidon. To test for antipyrine add a few more drops of sodium nitrite solution (e) and dilute sulfuric acid. A yellowish green solution remains, after the disappearance of the purple coloration due to pyrimidon, if antipyrine is present.

### QUANTITATIVE METHODS.

Pyrimidon has the characteristics of a basic substance as it combines with acids to form salts. Only traces of pyrimidon can be extracted from acid solutions with ether or chloroform. It can be readily extracted by ether, or chloroform from ammoniacal or sodium hydroxide solutions. The French Pharmacopœia states that pyrimidon is precipitated by picric acid. A quantitative method based on this reaction has been proposed in which the excess of a standard solution of picric acid is titrated back. It was found that picric acid does not precipitate pyrimidon in dilute solutions, so that the method is considered unsatisfactory for quantitative work. The French Pharmacopœia gives a quantitative titration method in which pyrimidon is titrated with standard acid using methyl orange as an indicator. The methods sub-

mitted below are based on these characteristics and a method has been devised whereby pyramidon is changed to pyramidon chloride and estimated from its chloride content.

### 1.—*Extraction Method.*

Dissolve an amount of the powdered sample containing about 0.2 gram of pyramidon in 10 cc. of 1% sodium hydroxide solution. Transfer to a separatory funnel. Extract the pyramidon with chloroform using 20 cc. for the first extraction and 15 cc. portions for three successive extractions. Transfer the chloroform solutions to another separatory funnel. Wash the chloroform by shaking with 5 cc. of distilled water. Filter the chloroform into a tared beaker. Wash the separatory funnels and filter paper with 10 cc. more of chloroform. Evaporate on top of a steam bath using an air current from an electric fan. Heat the solid residue for 5 minutes at 100°C. and transfer to a desiccator. Determine the weight of the residue and calculate as pyramidon.

### 2.—*Precipitation Method.*

Take an amount of pure pyramidon, or of the residue obtained by extraction with chloroform, as directed in Method 1, containing about 0.2 gram of pyramidon. Transfer to a tared beaker. Add an excess of 0.1N hydrochloric acid. Pyramidon hydrochloride is formed which is not volatile at 100°C. Evaporate to dryness on the steam bath to remove the excess of hydrochloric acid. Add 5 cc. of distilled water and evaporate to dryness again. Repeat the process two more times to insure complete removal of the excess of hydrochloric acid. Heat for one hour in a drying oven at 100°C. Transfer to a desiccator, cool and determine the weight of the residue. The amount of pyramidon present may be estimated by multiplying the pyramidon hydrochloride by the factor 0.8638. Dissolve the residue in distilled water. Add an excess of silver

## RESULTS OF ANALYSIS BY THE ASSOCIATE REFEREE.

### 1.—*Extraction method.*

WEIGHT OF SAMPLE	AMOUNT RECOVERED	
<i>gram</i>	<i>gram</i>	<i>per cent</i>
0.20	0.1983	99.1
0.20	0.1968	98.4
0.10	0.0995	99.5

### 2.—*Precipitation method.*

0.200	0.2002	100.1
0.200	0.2040	102.0
0.200	0.1968	98.4
0.200	0.2005	100.2

### 3.—*Titration method.*

0.50	21.0 cc. 0.1N acid	97.1
0.25	10.6 cc. 0.1N acid	97.0

nitrate and a few drops of nitric acid. Heat on a steam bath until the precipitate settles. Filter on a tared Gooch crucible. Wash the precipitate with hot distilled water and 5 cc. of 95% alcohol. Dry to constant weight at 100–110°C. The weight of the silver chloride found multiplied by the factor 1.6131 gives the weight of pyramidon present in the sample.

### 3.—Titration Method.

Dissolve 0.50 gram of pyramidon in 5 cc. of water. Add a few drops of methyl orange indicator and titrate with 0.1N hydrochloric or sulfuric acid. The 0.1N factor for pyramidon is 0.0231.

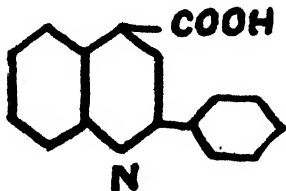
### RECOMMENDATION.

It is recommended that Method 1—extraction method—and Method 2—precipitation method—be studied by collaborators during the coming year.

## REPORT ON PHENYLCINCHONINIC ACID (CINCHOPHEN, ATOPHAN).

By WILLIAM RABAK<sup>1</sup> (U. S. Food and Drug Inspection Station, Minneapolis, Minn.), *Associate Referee*.

Phenylcinchoninic acid was first introduced into medicine under the proprietary name "Atophan". It was admitted into the United States Pharmacopœia, Ninth Revision, under the title "Acidum Phenylcinchoninicum". It is stated that it is "an organic acid, 2-phenyl-quinoline-4-carboxylic acid ( $C_{16}H_{11}O_2N$  or  $C_6H_5 \cdot C_9H_5N \cdot COOH = 249.10$ )". It was first described by Doebner and Gieseke<sup>2</sup> who prepared it by warming together pyroracemic acid, benzaldehyde and anilin in alcoholic solution. It has the following structural formula:



For the purposes of this investigation a commercial specimen of phenylcinchoninic acid was obtained and purified by recrystallization from 95 per cent alcohol. The molecular formula was then verified by the

<sup>1</sup> Presented by W. O. Emery.

<sup>2</sup> *Ann.*, 1887, 242: 290.

preparation of the platinum salt and subsequent analysis of the same. The theoretical composition of the addition product with platinic chloride is  $(C_{16}H_{11}NO_2 \cdot HCl)_2PtCl_4$ . Theoretically this compound contains a platinum content of 21.49 per cent. Actual analysis of the platinum salt prepared from the product employed in this investigation showed a platinum content of 21.20 per cent. This was accepted as sufficient proof that the empirical formula employed in the calculations in this method was correct. Melting point determinations further verified the authenticity of the product.

Various methods were studied in an attempt to develop a reliable method of estimation. In connection with this work it was found that the compound readily forms an iodine addition product. This comes down in the form of brown scales when 0.1N iodine solution is added to a warm solution of phenylcinchoninic acid in acetic acid. Attempts were made to develop a method of estimation along this line, but satisfactory results could not be obtained. Several metallic salts were also prepared in an attempt to find a compound, the solubility of which would permit of quantitative precipitation. The mercury, calcium, barium, and copper salts were prepared, but in each case the solubility was too great to allow quantitative estimation.

The greatest obstacle encountered in the development of a method for the estimation of phenylcinchoninic acid was its insolubility in ordinary solvents. Previous solubility determinations by the writer<sup>1</sup> indicated that the most suitable solvent is ethyl acetate. Its variable composition, however, made it unreliable for quantitative estimations. In searching for a more suitable solvent, it was found that boiling absolute ethyl alcohol was very efficacious, and because of its uniformity of composition and availability it was selected as being best adapted for this particular method.

Owing to the presence of the free carboxyl group, phenylcinchoninic acid displays distinct acidic properties. When treated with sodium hydroxide the hydrogen of the carboxyl group becomes displaced by sodium, forming the soluble sodium phenylcinchoninate. Likewise, when treated with ammonium hydroxide, the soluble ammonium salt is formed. No hydrolysis or decomposition occurs when this compound is treated with caustic alkali. Boiling under a reflux condenser with 0.5N alcoholic potassium hydroxide for a period of one hour was found to produce no effect on the alkali consuming power of phenylcinchoninic acid. Therefore, a quantitative titration of the carboxyl group was thought possible. To this end, the common indicators were tried, which resulted in the selection of phenolphthalein as being the best suited for quantitative titration of this compound. After a series of

<sup>1</sup> Annual Reports Chem. Lab. Am. Med. Assoc., 1918, 11: 73.



trials the following method was evolved as being reliable in the quantitative estimation of phenylcinchoninic acid in tablet and powdered form:

*Method of assay.*

Accurately weigh 1 gram of the powdered material and transfer to a 250 cc. Erlenmeyer flask by means of neutral absolute alcohol, using about 60 cc. to complete the transfer. Place on a boiling water bath and boil for 1 minute. Quickly decant through a rapid 12.5 cm. filter, catching the filtrate in a second 250 cc. Erlenmeyer flask. Repeat this operation twice, using 30 cc. of absolute alcohol each time. Rinse the flask thoroughly with boiling alcohol and finally wash filter and tip of funnel with 60 cc. of boiling absolute alcohol by means of a small wash bottle, carefully washing the upper edge of the filter paper. Add a few drops of phenolphthalein followed by 50 cc. of 0.1N sodium hydroxide (excess) and titrate with 0.1N acid until the pink color just disappears. Subtract the number of cc. of acid used from the cc. of alkali added. Each cc. of 0.1N alkali consumed corresponds to 24.91 mgs. of phenylcinchoninic acid.

## REPORT ON CHLORAMINE-T.

By W. H. HEATH (U. S. Food and Drug Inspection Station, Buffalo, N. Y.), *Associate Referee.*

### HISTORY.

Numerous attempts have been made to use the germicidal properties of chlorine, which have been known for many years to surgeons, particularly for the purposes of irrigation after surgical operations. There have been many difficulties to overcome, due principally to the irritating and caustic properties of the most readily available forms.

One of the early forms of application was a solution of sodium hypochlorite, but caustic properties occasioned the addition of boric acid in an attempt to neutralize the alkali. Kastle, Keiser and Bradey<sup>1</sup> reported the manufacture of organic chloramines. Chattaway<sup>2</sup> further described them.

The first practical demonstration of the uses of these organic chloramines was reported by Dakin and his associates<sup>3</sup>.

### METHOD OF MANUFACTURE.

Two forms of chloramine are found in general use—chloramine-T and dichloramine-T. The former is sodium paratoluenesulfochloramide and is soluble in water; the latter is paratoluenesulfonatedichloramide and is

<sup>1</sup> *Am. Chem. J.*, 1896, 18: 491.

<sup>2</sup> *J. Chem. Soc. Trans.*, 1905, 87: 145.

<sup>3</sup> *J. Am. Med. Assoc.*, 1917, 69: 27.

practically insoluble in water, the usual method of administration being in solutions of chlorinated paraffine oil or chlorinated eucalyptol.

Practically all surgeons now use the dichloramine-T, because of the slow and even liberation of chlorine upon the solution coming in contact with the exudations from suppurating wounds.

The base used in the manufacture of these products is usually paratoluenesulfochloride, a by-product in the manufacture of saccharin. This is boiled with ammonium carbonate and treated with a strong solution of sodium hypochlorite. The sodium salt is then salted out and dried.

These two chemicals, as well as their solutions, decompose readily, with the formation of hydrochloric acid, and cause irritation to the skin.

The following tests for identity and purity are suggested for collaborative work on this subject. They are reported in New and Non-official Remedies, 1921, or were suggested by H. McCausland of the Abbott Laboratories.

#### CHLORAMINE-T.

One gram of chloramine-T is soluble in about 7 cc. of boiling water. Chloramine-T is insoluble in chloroform, ether and benzol.

Chloramine-T melts at 160–185°C., with decomposition.

In neutral solutions chloramine-T liberates iodine from iodides, but not bromine from bromides; when acidified with hydrochloric acid the bromine will be liberated.

#### *Quantitative determination of available chlorine.*

Dissolve 0.3 to 0.5 gram of chloramine in 50–100 cc. of distilled water. Add 10 cc. of potassium iodide test solution and 10 cc. of dilute acetic acid, and titrate the liberated iodine with 0.1M sodium thiosulfate, using no indicator. Each cc. of thiosulfate consumed represents 0.014 gram of chloramine-T.

#### DICHLORAMINE-T.

Dichloramine melts at 81°C.

One gram of the sample is completely soluble in 1 cc. of chloroform. At times there is a slight precipitation of the insoluble amide decomposition product.

The strong odor of the hydrochloric acid or chlorine indicates decomposition of the product. This may be confirmed by holding a congo red test paper over the product so that the action of such decomposition is shown by the paper. A test has been suggested to show the presence of chlorine or hydrochloric acid in the product, by shaking a portion of dichloramine with water, filtering and testing the resultant filtrate with silver nitrate solution. There is a slight solubility of dichloramine in water which renders this test impracticable.

*Quantitative test for available chlorine.*

Dissolve 0.15 gram of dichloramine-T in 5 cc. of glacial acetic acid, add 10 cc. of the 10% solution of potassium iodide, and titrate with 0.1N sodium thiosulfate, using no starch indicator. 1 cc. of 0.1N thio is equivalent to 0.0060 gram of dichloramine-T.

RECOMMENDATION.

It is recommended that the study of the method for the analysis of chloramine products be continued next year, and that the tests which have been suggested in this report be submitted for collaborative work.

## SECOND DAY.

### THURSDAY—MORNING SESSION.

#### REPORT ON REAGENTS.

By G. C. SPENCER (Bureau of Chemistry, Washington, D. C.), *Referee*.

Out of a total of 183 chemicals purchased for stock by the Bureau of Chemistry during the past year, only 8 were rejected as being unsatisfactory.

In most cases rejected shipments are returned to the factory, but instances have been known of their resale to neighboring laboratories where no inspection was made.

Continual watchfulness is necessary to keep reagents up to a proper standard for high-grade work, as may be seen in the following statements.

#### ACETIC ACID.

In one case, glacial acetic acid was bought with the stipulation that it should be 99.9 per cent acid strength. Assay by the freezing-point method showed a strength of only 99.7 per cent. The manufacturer, depending upon an assay by titration, was unable to see what was wrong until he was informed of the Bureau's method. With this information he had no trouble in preparing an acid of the desired strength.

#### FUMING SULFURIC ACID.

A sample of fuming sulfuric acid claimed to be 50 per cent strength was found to contain less than 27 per cent of sulfur trioxide.

#### SULFURIC ACID.

One shipment of sulfuric acid had to be rejected because of low acidity and also because it contained too much arsenic and residue.

#### HYDROCHLORIC ACID.

An order of hydrochloric acid, satisfactory in other respects, was about 5 per cent too low in acid value. A protest to the manufacturer brought an offer to adjust the price according to the acidity.

**MAGNESIUM OXIDE.**

Magnesium oxide was found to contain sulfur which is often present in this chemical.

**CHLOROFORM.**

One hundred nine chloroform samples that had been packed in tin containers for more convenient shipment were in all cases found to be below the U. S. P. standard of purity. Some of these were originally intended for use in the American army in France for anesthetic purposes. Contrary to expectations, however, a reaction developed between the metal container and the chloroform, with the result that the chloroform assumed a turbid appearance and gave signs of organic as well as inorganic contamination. Moreover various cans showed different colored sediments which indicated the presence of uncertain amounts of tin, lead, and iron compounds. The chloroform itself was sometimes acid in reaction, sometimes strongly reducing, and in all cases had a distinctive foreign odor. To what extent these impurities can be characterized remains to be seen, but in any case the practice of packing chloroform in tins has been definitely abandoned.

**ACTIVATED LIME.**

Your attention is called to a new form of calcium oxide known as "activated" or "reheated" lime. It is prepared by slaking certain grades of quicklime with water, then heating the calcium hydroxide at red heat for about two hours. This treatment re-forms calcium oxide in a powdered condition, which, owing to its greater contact surface, is more reactive than the usual calcium oxide. All investigational work on this subject has thus far been done by F. C. Mathers<sup>1</sup> at the University of Indiana, the project being sponsored by the National Lime Association. It has been difficult for the Bureau of Chemistry to purchase satisfactory calcium oxide for reagent purposes for a number of years, and it is believed that this material may prove to be an acceptable innovation. Some of the applications already indicated for this lime are the dehydration of transformer oil, the dehydration of petroleum, and the preparation of absolute alcohol.

**ACETIC ANHYDRIDE.**

An original quantitative analytical method for the determination of acetic anhydride has been prepared by the referee, and the manuscript has been recommended by the Bureau of Chemistry for approval for publication. The proposed method was presented in a separate paper before the Drug Section<sup>2</sup>.

<sup>1</sup> *Rock Products*, 1922, 25: 83.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 493.

## LOEB COLLECTION.

It may be of interest to make reference at this time to the Loeb collection of original chemical types which has been recently installed in the Old National Museum building in this city. This collection, maintained by the proceeds of a bequest by the late Morris Loeb of New York City, provides a permanent storage for original chemical compounds made in America. These specimens are mounted in sealed glass tubes and are carefully catalogued. Future investigators will have the privilege of comparing compounds that they may be studying with these samples, and, in disputed or doubtful cases, the tubes may be opened for the purpose of withdrawing small amounts of the deposited specimens for crystal measurements or for mixed melting-point determinations. The samples of the collection are always available for inspection by visitors on request in the Division of Textiles. At the present time only a few specimens have been filed.

## RECOMMENDATION.

It is recommended that the work on reagents be continued as formerly, and that the members of the association cooperate as fully as possible with the referee in maintaining high standards of purity and dependability for chemicals.

The Referee on Non-alcoholic Beverages and on Flavoring Extracts recommended that the work be combined under the heading "Beverage and Household Flavors and Non-alcoholic Beverages". Committee C approved this recommendation inasmuch as the character of the work on flavoring extracts at the present time is principally in connection with these summer beverages.

REPORT ON NON-ALCOHOLIC BEVERAGES AND  
FLAVORING EXTRACTS.

By W. W. SKINNER (Bureau of Chemistry, Washington,  
D. C.), *Referee*.

No cooperative work on these subjects has been conducted during the year. The referee has kept in touch with and abstracted the literature, with a view to initiating plans for future work. With regard to the literature on non-alcoholic beverages, only a few articles of an analytical nature have appeared in the last two years. Of these, a method by A. Azadian for the determination of caffeine<sup>1</sup> may be mentioned. This method depends upon the use of the so-called Bertrand's reagent, which

<sup>1</sup> *Bull. soc. chim. belg.*, 1922, 31: 15.

is prepared by dissolving 5 grams of silico-tungstic acid in 100 cc. of water. The sensibility of the reaction is 1 to 50,000. The precipitate which is formed in the reaction is ignited, and the weight of the precipitate when multiplied by 0.2646 gives the weight of the caffeine. The method can be applied to tinctures and fluid extracts of the cola nut.

A method for the detection of apple juice in so-called pure fruit jams<sup>1</sup> may be applied to beverages. The author, M. C. F. Muttelet, gives a method for the determination of malic acid by precipitation as the barium salt, the separation of the barium salts of malic and citric acids through difference of solubility in water, and the final conversion of the barium malate to barium sulfate, weighing as such.

In an article appearing in the Journal of the American Chemical Society<sup>2</sup>, the presence of methyl anthranilate in commercial grape juice is established. The authors, Power and Chesnut, state that they found up to 2 milligrams per liter of the ester in juices of the Concord type, and in most cases less than 0.2 milligram per liter in the lighter colored juices. In a previous article<sup>3</sup>, the authors described a method for the detection of methyl anthranilate in fruit juices.

Several methods for analyzing flavoring extracts have appeared in the literature recently. Among these is a method for the determination of the lead number in vanilla extracts<sup>4</sup>, a modification of the well-known official method<sup>5</sup>. It differs from the official method in that the alcohol is removed by distillation, and the lead precipitate is formed in hot solution, thus gaining equilibrium at once and reducing the time necessary for settling. Through these modifications the determination of alcohol is made on the same portion as the lead number, and much time is saved. The color values of the filtrate must be dispensed with, but it has been found that upon dilution an extract gives a lead number proportional to its dilution, which is not the case with the official method. The figures obtained by the new method are generally higher and more consistent than those obtained by the official method.

A method for the determination of vanillin in vanilla extracts which excludes the vanillin oxidation products has been published<sup>6</sup>. The authors, Bowers and Moyer, believe that the flavor of vanilla extracts is changed by the oxidation of the vanillin present. Methods now in use do not show the true vanillin content but include these oxidation products as well. Bowers and Moyer suggest a combination of the Folin and Denis<sup>7</sup> method with the Estes<sup>8</sup> method. The former, they

<sup>1</sup> *Ann. fals.*, 1922, 15: 196.

<sup>2</sup> *J. Am. Chem. Soc.*, 1921, 43: 1741.

<sup>3</sup> *Ibid.*, 377.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1921, 13: 414.

<sup>5</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 198.

<sup>6</sup> Special Bulletin, Food Department, North Dakota Agricultural College, 1920, 5, No. 16: 518.

<sup>7</sup> *J. Ind. Eng. Chem.*, 1912, 4: 670.

<sup>8</sup> *Ibid.*, 1917, 9: 142.

say, eliminates the oxidation products, and the latter gives a more desirable color for comparison.

Folin and Denis precipitate the interfering substances by diluting the extract and adding a mixture of normal and basic lead acetates. The Estes method employs a solution of mercury in nitric acid which gives a purple color with vanillin quantitatively.

A method for the determination of esters in imitation flavoring extracts has also been published<sup>1</sup>. The author, George F. Beyer, shows that recovery of esters is not complete in the case of the more complex esters when the distillation is carried out in the usual manner. However, he finds that practically complete recovery of all esters is accomplished if the distillation is made from a medium of 50 per cent alcohol instead of from water.

#### RECOMMENDATIONS.

It is recommended—

(1) That as the subjects of non-alcoholic beverages and of flavoring extracts are closely allied they be combined under one subject, such as "Beverage and household flavors and non-alcoholic beverages". The term "flavor" is preferred to the term "flavoring extract", since from the standpoint of the enforcement of the Federal Food and Drugs Act the two terms are not synonymous. The term "flavor" is considered to be much broader, and the term "flavoring extract" to be limited to those flavors which have a menstruum of ethyl alcohol of proper strength.

(2) That the referee for next year give consideration to methods of analysis for non-alcoholic flavors such as, for example, determination of the quantity of orange oil in peanut oil and in mineral oil.

No report was made on eggs and egg products as no referee was appointed.

#### DETERMINATION OF ZINC AND COPPER IN GELATIN AND GLUE.

By RAYMOND HERTWIG (U. S. Food and Drug Inspection Station, San Francisco, Calif.).

The examination of gelatin for zinc and copper is frequently required of the food analyst. Two methods commonly used are the tentative method of the Association of Official Agricultural Chemists<sup>2</sup> for determining metals in foods in general, and an unpublished method of the New York Food and Drug Station, devised for gelatin in particular.

<sup>1</sup> *J. Ind. Eng. Chem.*, 1922, 14: 324.

<sup>2</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 151.



In the tentative method of the association, the organic matter is destroyed by digestion with nitric and sulfuric acids. This oxidation is slow and difficult to control. Very obnoxious fumes are formed and much strong acid must be neutralized. The method is accurate, but it is not satisfactory for routine analysis.

In the New York Station method, 50 grams of the sample are first hydrolized with 200 cc. of 10 per cent hydrochloric acid. After neutralizing with ammonia, sodium phosphate is added, followed by an excess of magnesia mixture to facilitate filtration. The whole is then saturated with hydrogen sulfide, and the precipitate obtained is treated with 75 cc. of 4 per cent hydrochloric acid. This leaves the copper sulfide undissolved, and from this precipitate the copper is determined volumetrically. The iron present is removed by the basic acetate method, and the zinc is precipitated from the filtrate with hydrogen sulfide and finally weighed as zinc oxide.

Author's comment.—When much insoluble gelatinous keratin is present the first filtration is attended with difficulty. The extraction of the zinc from the first precipitate is slow as is also the digestion of the copper sulfide and filter paper with nitric and sulfuric acids. This method has been found too elaborate and time-consuming for routine work.

A simpler method than either of these methods is described below.

#### *Proposed Method.*

Place 20 grams of sample in a platinum or silica dish, cover with a small filter paper, and heat on an asbestos gauze until the gelatin is charred. (Do not allow the dish at this time or subsequently to be exposed to a heat higher than faint redness.) Complete the ashing in an electric muffle furnace. (The ashing may be hastened by leaching the well-charred mass with hot water.) Digest the ash with 20–30 cc. of hot hydrochloric acid (1 volume of acid to 1 volume of water) for a few minutes and filter into the first water leachings. Neutralize the solution with ammonium hydroxide, using methyl orange, and add sufficient excess to precipitate all iron, aluminum, etc., and assure solution of all zinc and copper as complex ions. Heat the solution to about 80°C., filter, and wash the precipitate with a 3% solution of ammonium chloride, containing about as much free ammonium hydroxide as the original solution. Neutralize the filtrate with concentrated hydrochloric acid and add an excess of 5 cc. for each 100 cc. of solution. Add a little well-disintegrated filter-paper pulp to the hot solution, stir well to distribute it, and pass in hydrogen sulfide until the solution is cold. Stir the solution at intervals to collect traces of the copper sulfide on the pulp. Filter out the copper sulfide, observing the necessary precautions to prevent its oxidation, and wash with 3% ammonium chloride solution saturated with hydrogen sulfide.

Dissolve the copper sulfide on the filter paper by washing with 25 cc. of boiling hot nitric acid (1 volume of acid to 3 volumes of water). Pass the hot filtrate through the filter twice more and wash with hot water. Determine the copper in the filtrate by the official volumetric method<sup>1</sup>.

Neutralize the filtrate containing the zinc with ammonium hydroxide, make slightly acid with dilute hydrochloric acid (2.5N) and add 1 cc. excess. Add 10–15 cc. of 50%

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 79.

ammonium acetate solution. Pass hydrogen sulfide into the cold solution until the zinc is completely precipitated. Filter the zinc sulfide on a Gooch, wash with a 2% ammonium nitrate solution saturated with hydrogen sulfide, and burn to constant weight. Weigh as zinc oxide.

Comparative results by the three methods are given in the table. Twenty-gram samples were used in each method.

*Determination of copper and zinc by different methods.*

SAMPLE	ZINC OXIDE			COPPER	
	N. Y. METHOD	A. O. A. C. METHOD	PROPOSED METHOD	N. Y. METHOD	PROPOSED METHOD
	gram	gram	gram	gram	gram
Glue No. 1.....	↑ .....	0.0171 0.0172	0.0168 0.0173	None	None
Glue No. 1*....	..... .....	0.0171 0.0172	0.0169 0.0172	..... .....	0.0194 0.0196
Gelatin No. 1...	0.0107 0.0109 .....	..... ..... .....	0.0108 0.0109 0.0109	None ... .. .....	None ..... .....
Gelatin No. 2...	0.0056 0.0058	..... .....	0.0074 0.0082	None .....	None .....
Gelatin No. 3...	0.0180 0.0195	..... .....	0.0222 0.0224	0.0015 0.0015	0.0014 0.0016

\*Twenty grams of Glue No. 1 to which was added 0.0202 gram of copper as copper nitrate before ashing.

†Impossible to filter after acid hydrolysis.

### CONCLUSION.

A simple method is proposed for determining zinc and copper in gelatin and glue. It is recommended as more satisfactory for routine work than either the tentative association method or the so-called New York Station method, and is much simpler and more rapid than either. The results appear to be equally dependable. The method has also been found applicable to dried eggs.

### REPORT ON SACCHARIN.

By M. G. WOLF (U. S. Food and Drug Inspection Station, New York, N. Y.), *Referee*.

Your referee experimented with two methods. One was along the line suggested at the last A. O. A. C. meeting and dealt with the determination of small amounts of saccharin in bread-stuffs; the other was used with saccharin in products containing mustard. The first method proved unsatisfactory in that no means have so far been devised which

have been successful in obtaining more than about 50 per cent of the saccharin, owing, largely, to interference of gluten in the extraction of the material, but possibly to the fact that part of the saccharin added may be decomposed by the heat employed in preparing the bread.

The second line of research has been more productive of results, and if the work is continued the new method, which depends upon the precipitation of the nitrogen component in the saccharin as the chloroplatinate, will undoubtedly justify the effort.

It is recommended that the work be continued another year.

## REPORT ON COLORING MATTERS IN FOODS.

By L. A. BURNS<sup>1</sup> (U. S. Food and Drug Inspection Station,  
St. Louis, Mo.), *Referee*.

Three samples of mixtures of colors were sent to five analysts who had previously signified their willingness to collaborate on color work. Of these five only one, E. H. Berry of the Chicago station, replied.

In the instructions to the collaborators attention was called to the fact that it was desired that the methods as adopted tentatively at the 1920 meeting of the association<sup>2</sup> be studied carefully. It was requested that suggestions on ways of improving these methods be submitted. Berry suggested that the instructions for determining sulfate might be condensed under one heading. W. O. Brewer of the Calco Chemical Company signified his willingness to cooperate. He stated that the instructions as outlined in the methods were not plain, and that the interpretation might not be the same by two different persons. He further suggested the meeting of representatives from various concerns interested and chemists in charge of color investigation in order to iron out any portion of the instructions which is vague or indefinite. In line with this suggestion, Joseph A. Ambler, chemist in charge of the Color Laboratory, has requested that any criticisms or suggestions for the betterment of the tentative methods be communicated to him. The manufacturers have been given the same instructions.

In view of the fact that the Color Laboratory is planning to undertake the work of revising the chapter on Coloring Matters in Foods<sup>3</sup> in order to make it more condensed and explicit, it is recommended that the Referee on Coloring Matters in Foods confine his work for the ensuing year to the analysis of colors as follows:

1. Separation and identification of water-soluble permitted and non-permitted dyes.
2. Separation and identification of oil-soluble dyes.

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<sup>1</sup> Presented by R. A. Doolittle.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 196.

<sup>3</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 131.

## A PRELIMINARY REPORT ON THE PRESENCE OF PRIMARY AMINES IN CANNED MUSHROOMS.

By CHARLES F. JABLONSKI<sup>1</sup> (U. S. Food and Drug Inspection Station, New York, N. Y.).

In the course of examination of canned mushrooms for added coloring matter a rather unexpected reaction was observed. It was noted that the yellow supernatant liquid behaved like most vegetable coloring matters, *viz.*, no appreciable dyeing on wool or cotton; no distinct actions of acids or alkalies, save that of increasing or decreasing the tint a slight amount; no action with stannous chloride or other reducing agents; and no stripping or redyeing. However, when a portion of the original liquid was acidified with hydrochloric acid, diazotized, and coupled with an alkaline solution of alpha-naphthol an orange-red color was obtained. In order to determine whether the same reaction would be obtained from the drained mushrooms, some of them were passed through a chopper and extracted with 80 per cent alcohol made slightly alkaline with ammonia. After 24 hours the yellow alcoholic solution was filtered and evaporated until the ammonia was expelled; the dyeing and coupling reactions were repeated, and the same results were obtained. Several other brands of bleached and unbleached mushrooms were examined, and all gave similar results.

After these preliminary experiments a more comprehensive study was deemed necessary. With that end in view, a sample of canned mushrooms was drained, and the mushrooms were passed through a chopper and extracted as before with slightly ammoniacal 80 per cent alcohol. After 24 hours the alcoholic solution was filtered and evaporated until the ammonia was expelled. Pieces of wool were boiled in portions of the original drained liquor, slightly acidified, and also in the alcoholic solution obtained by extracting the chopped mushrooms. Very little color, of a brownish yellow shade, was absorbed by the wool in both instances. Both acids and alkalies spotted the dyed wool yellow. Neither the drained liquor nor the alcoholic extract obtained from the mushrooms was extracted by solvents in any appreciable amount. However, by treating portions of these solutions with a few drops of hydrochloric acid, diazotizing, and coupling with an alkaline solution of alpha-naphthol, an orange-red color was obtained which was separated into two component colors, one ether soluble and the other water soluble, in the following manner:

The orange-red solution was extracted with ether, and the aqueous layer was set aside. The ether layer was washed several times with water, transferred to a casserole,

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<sup>1</sup> Presented by H. W. Redfield.

and evaporated off. After being taken up with alcohol a piece of silk immersed in it was dyed a yellow color. The spot tests of this silk were as follows:

Concentrated hydrochloric acid = reddish violet;  
 Concentrated sulfuric acid = dark blue;  
 Sodium hydroxide, 10% = red; and  
 Ammonium hydroxide (concentrated) = no change.

The aqueous layer, which had been set aside, was acidified slightly with hydrochloric acid and extracted with amyl alcohol. This amyl alcohol solution was washed several times with water, and the color was finally transferred into water by means of gasoline. A piece of wool dyed in this orange-colored water solution gave reactions similar to Orange I, S. & J. No. 85. From this it would appear that a small amount of aniline or sulfanilic acid or of both is present in canned mushrooms.

About 20 samples of canned bleached and unbleached mushrooms were examined, and in every instance the same reactions were observed. The only difference noted between the bleached and unbleached varieties was that the bleached gave a greater amount of water-soluble dye and a proportionally smaller amount of ether-soluble dye. The reverse was noted with the unbleached mushrooms.

Additional investigation is being made.

## REPORT ON METALS IN FOODS.

By W. F. CLARKE (Bureau of Chemistry, Washington, D. C.), *Referee*.

### TIN.

Owing to the demands of other work, your referee found it impossible to arrange for cooperative work as was recommended with reference to the modification of the Penniman method<sup>1</sup>. However, some further study of it has been made and minor modifications have been tested.

In its present status the method may be briefly outlined as follows:

In a 1-liter Pyrex Erlenmeyer flask destroy by acid digestion the organic matter in 50 grams of the food material under examination; dilute with 100 cc. of water and neutralize with strong sodium hydroxide solution. Dilute with water to 350 cc., add 8½ cc. of concentrated sulfuric acid, and then add, on the steam bath, at 80°C., 20 grams of zinc powder (20 or 30 mesh). Let the action continue for one hour. Remove from the bath and let stand overnight. At the end of this period replace on the bath and, at 80°C., complete the precipitation of the tin by treating for 15 minutes with 2 grams of iron powder (reduced by hydrogen). Filter immediately by decantation through an asbestos nest built on a 5 or 6 mm. Witt plate in a glass funnel. Wash twice, decanting through the asbestos. Remove the asbestos, skin off the outside layers as much as practicable, and place the nest in the Erlenmeyer. By means of a suitable

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 28.

stopper lead through the flask a stream of carbon dioxide, and through a dropping funnel in the stopper add 150 cc. of concentrated hydrochloric acid. Cause the acid to fall drop by drop on the asbestos until the nest is thoroughly disintegrated; wash down the sides of the flask, insuring the reduction of any oxidized iron by contact with the nascent hydrogen being liberated; and finally add the remainder of the acid in a stream rapidly, but avoiding too violent action. Boil to dissolve the metals, cool, and add rapidly through the dropping funnel 200 cc. of a previously boiled and cooled mixture of 1 to 1 concentrated ammonia and water. After cooling, titrate with approximately 0.02N iodine solution, keeping the carbon dioxide flowing in through a tube inserted in the mouth of the flask. Standardize the iodine by means of a range of weighed, pure, tin-foil samples approximating 20 mg., 50 mg., and 100 mg. If the sample to be tested is very high in tin content a charge smaller than 50 grams may be taken, or the iodine solution may be standardized with a corresponding weight of tin-foil.

### PROCEDURE.

Without the addition of organic material, weighed amounts of tin dissolved in concentrated hydrochloric acid were digested with nitric and sulfuric acid, the treatment being continued until the sulfuric acid fumed heavily. From this stage the outlined method was followed. The accuracy attained is indicated as follows:

TIN TAKEN	IODINE REQUIRED	RATIO OF IODINE SOLUTION TO TIN	
<i>mg.</i>	<i>cc.</i>	<i>cc.</i>	<i>mg.</i>
5.0	4.85	1	1.031
10.2	9.90	1	1.030
20.2	19.90	1	1.015
50.0	49.65	1	1.007
100.3	99.30	1	1.010
100.1	98.64	1	1.015
		Avg. 1	1.018

If, owing to the liability to a high percentage error in weighing, the first two determinations be omitted, the maximum deviation of the determinations is less than 1 per cent.

The above modification of this method contains only one feature of the original Penniman procedure, and even in that respect it has been altered, that is the zinc precipitation of the tin has been rendered more nearly complete by means of an additional charge of iron. It is thought that it might better be called the zinc-iron precipitation method.

### RECOMMENDATION.

It is recommended that the zinc-iron precipitation method for the determination of tin, as described in this report, be studied.

## REPORT ON ARSENIC IN FOODS.

By R. M. HANN (Bureau of Chemistry, Washington, D. C.), *Associate Referee*.

The two recommendations of the referee for 1922<sup>1</sup> were studied and are described in detail.

*The Farr<sup>2</sup> modification of the Gutzeit method.*

The further study of the Farr method, as yet unpublished, has confirmed last year's results, in that the procedure recommended has been demonstrated to be accurate for the determination of arsenic in concentration below 20 micromilligrams. There is no doubt but that the modification could be used to advantage in the analysis of drugs, pharmaceuticals, chemicals, etc., to establish the arsenic content above or below some definite limit.

It may be noted, however, that the method, as it now stands, is open to several objections, the principal one of which—probably uncorrectable—is the increasing difficulty of distinguishing color intensity of successive determinations when the arsenic content increases in micro-milligram units much beyond the limit of twenty, and further it has been observed that the rapidity of evolution of hydrogen has marked effects upon stains prepared under identical conditions. The apparatus itself is not well suited for laboratory manipulation, the fading of stains and the uncertainty of obtaining a uniform absorbent paper presenting difficulties which stand in the way of its adoption as a general method. Finally, it may be stated that the present tentative Gutzeit method is now so generally accepted that it is doubtful if this modification would ever gain any considerable following among the analysts doing arsenic work.

## THE PRESENT TENTATIVE GUTZEIT METHOD.

The determination of arsenic by various modifications of the Gutzeit method has been made a subject of study by referees of this association since the appointment of a Referee on Metals in Foods. The introductory study was undertaken by Loomis<sup>3</sup>, and under his direction the Sanger and Black<sup>4</sup> procedure, as modified by C. R. Smith<sup>5</sup>, gave very good results, though difficulty was experienced with the hydriodic acid reduction and with the strength of the acid used. These factors were carefully considered by Treuthardt in the two following years<sup>6</sup>, and it was recommended that the variable factors affecting evolution—con-

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 34.

<sup>2</sup> H. V. Farr, Mallinckrodt Chemical Works, St. Louis, Mo.

<sup>3</sup> U. S. Dept. Agr. Bur. Chem. Bull. 162: 139; *J. Assoc. Official Agr. Chemists*, 1915, 1: 244.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1907, 26: 1115.

<sup>5</sup> U. S. Dept. Agr. Bur. Chem. Circ., 102, 1912.

<sup>6</sup> *J. Assoc. Official Agr. Chemists*, 1915, 1: 530; 1917, 3: 43.

centration of solution, strength of acid, temperature, amount of zinc surface, condition of zinc, and time allowed for evolution—be ascertained and introduced in order to make the method more uniform. Klein<sup>1</sup> then took up the subject and, with the assistance of J. J. Doyle, reached certain conclusions in regard to the conditions which produced discordant results. Collins<sup>2</sup>, the succeeding referee, took exception to portions of Klein's work and advised adherence to the original details in the majority of cases. The writer, following Clarke's<sup>3</sup> recommendation in 1920, studied the Farr modification, which included the older technique of passing the evolved arsine through the sensitized paper.

#### THE QUESTION OF HYDRIODIC ACID REDUCTION.

The question of the use of potassium iodide has been discussed pro and con by previous referees and their assistants. The first collaborative study of the method yielded a number of conflicting opinions concerning the necessity, or even the advisability, of using potassium iodide. The question was apparently satisfactorily settled by Treuthardt and his co-workers in favor of the reduction, when Klein, following a nine months' study, stated that the presence of potassium iodide offered no advantage in the procedure and summarily discontinued its use. This step, however, was not advisable, as workers having a wide experience in the use of the method have shown the reduction to be incomplete in the case of refractory substances when the potassium iodide is omitted. At this point it may be stated that the function of stannous chloride is primarily that of an accelerator.

In an effort to clear up the variety of conditions met in arsenic work a questionnaire was sent out to about 20 analysts. The majority favored the addition of potassium iodide. Two analysts considered the reducing agent unnecessary, and, in regular routine analysis, did not warm up the solution to 90°C. before the determination.

It has been the experience of the present referee, as well as of a number of collaborators, that the addition of potassium iodide is an essential step to cause complete evolution of the arsine. Moreover, its value is increased, since a uniform, deep brown stain, which terminates sharply at its upper extremity, is obtained when the reduction is properly carried out.

The results shown in Table 1 support the contention that the hydriodic acid reduction serves to effect an increased evolution of arsine. The work was done by Raymond Hertwig, of the San Francisco Station of the Bureau of Chemistry, with arsenic solution obtained from sprayed fruit.

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1920, 3: 512; 4: 172.

<sup>2</sup> *Ibid.*, 1921, 4: 454.

<sup>3</sup> *Ibid.*, 1921, 5: 219.



TABLE 1.  
*Results showing advantage of using potassium iodide.*  
 (Expressed as micromilligram of arsenic trioxide per gram.)

QUANTITY USED	WITHOUT POTASSIUM IODIDE	WITH POTASSIUM IODIDE
cc.		
1	4	6
2	8	10
3	14	20

Hertwig comments as follows:

The solution used contained arsenic obtained by dissolving the arsenical spray from apples. The spray had been dissolved with concentrated nitric acid, the acid boiled off, and the solution made up to 100 cc. In the work done higher results were obtained in the determination where potassium iodide was used. Possibly the potassium iodide is necessary fully to reduce the arsenate.

It has also been the experience of E. H. Berry, Food and Drug Inspection Station, Chicago, Ill., that omission of potassium iodide gave low results—in fact, the dye samples analyzed by him showed only a slight trace of arsenic.

The results shown in Table 2, obtained by the writer, seem to substantiate the above conclusion. Identical procedures were followed in the analyses, except with respect to the addition of potassium iodide.

TABLE 2.  
*Results showing influence of the addition of potassium iodide.*  
 (Expressed as micromilligram of arsenic trioxide per gram.)

SUBSTANCE USED (10 gram sample)	WITHOUT POTASSIUM IODIDE	WITH POTASSIUM IODIDE
Erythrosine . . . . .	3	5
Indigotine . . . . .	2	12
Ponceau 3 R . . . . .	Blank	2
Orange I . . . . .	5	6
Erythrosine (356) . . . . .	15	19
Amaranth . . . . .	10	16
Baking Powder . . . . .	1	6
Baking Powder . . . . .	1	4
Phosphoric Acid . . . . .	3	5
Calcium Phosphate (5 mmg. As <sub>2</sub> O <sub>3</sub> added) . . .	3	6

In regard to the effect of potassium iodide on the condition of the stain, Berry<sup>1</sup> states that its use as a reducing agent is advantageous in that it makes it easier to obtain uniform stains on the mercuric bromide paper. This early observation was confirmed throughout the experience of the present referee and also by members of the Color Certification

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1915, 1: 583.

Laboratory of the Bureau of Chemistry, where the potassium iodide reduction is constantly used in the routine analysis of many organic products with entirely satisfactory results.

While it seems to be possible to analyze correctly solutions free from organic matter, phosphates, and like refractory substances without potassium iodide, the foregoing discussion and results indicate that its use is advisable in the majority of cases, and that it should be retained in the method.

#### THE USE OF HYDROCHLORIC ACID.

Early in the arsenic work of the association the question of the substitution of hydrochloric acid for sulfuric acid in the generation of hydrogen was advanced by Ginsberg<sup>1</sup>. Following his extensive study of the arsenic method, Klein<sup>2</sup> announced that either of the acids would serve the purpose equally well, and his contention was given weight by the later work of Collins<sup>3</sup>, who published results covering a great number of determinations.

Answers to the questionnaire, regarding the use of hydrochloric acid, indicated a unanimous vote in favor of its introduction as a reagent in the Gutzeit procedure. Many laboratory workers now use it almost exclusively in this class of work, while others prefer sulfuric acid following the oxidation of the organic material. The halogen acid possesses a decided advantage in that conditions of reduction are without appreciable effect upon it, while with sulfuric acid the variable conditions must be regulated to conform to certain limits to prevent the excessive evolution of hydrogen sulfide. These considerations and the extensive use of hydrochloric acid recommend its adoption as an alternative acid.

#### COLLABORATIVE WORK.

Collaborative work this past year has consisted mainly in the analyses of dyes. These were supplied by the Color Laboratory, Bureau of Chemistry. Since dyestuffs are of a complex organic nature and contain arsenic in small amounts in both soluble and insoluble conditions, it was considered that results obtained by collaborative study would settle finally any question pertaining to the accuracy of the method. The results are shown in Table 3.

Collaborative work upon the various commercial phosphoric acids<sup>4</sup> was also undertaken for the Bureau of Soils. The tentative method proved entirely satisfactory.

Correspondence with A. McGill, Chief Government Analyst of the Canadian Department of Health, concerning arsenic analytical pro-

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1917, 3: 46.

<sup>2</sup> *Ibid.*, 1920, 3: 512.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1918, 10: 860.

<sup>4</sup> *Ibid.*, 1922, 14: 533.

cedure, gave the information that the Gutzeit method, as employed by this association, had given very satisfactory results in the hands of that organization.

R. S. Hollingshead, of the Food and Drug Inspection Station, New Orleans, La., reported that he had had no trouble whatever with the Gutzeit method when the blank and unknown tests were made under identical conditions.

TABLE 3.  
*Collaborative results on the determination of arsenic in dyes.*  
(Expressed in micromilligram of arsenic trioxide per gram.)

COLLABORATOR	NAPHTHOL YELLOW S	PONCEAU 3 R	ORANGE I	AMARANTH	ERYTHROSINE B
E. H. Berry	0.5	0.5	1.0	1.0	...
H. Johnson Warner Jenkinson Co. St. Louis, Mo.	0.4	0.7	0.6	0.3	1.5
M. J. Goss Bureau of Chemistry Washington, D. C.	0.3	0.7	0.4	0.5	0.7
O. L. Evenson Bureau of Chemistry Washington, D. C.	0.3	0.7	0.4	0.7	0.5
L. A. Piquet National Aniline Co. Buffalo, N. Y.	0.4	0.4	0.4	0.4	1.0
R. M. Hann	0.5	0.7	0.5	0.5	1.6
Average.....	0.4	0.6	0.5	0.6	1.0

D. M. Walsh, Chief of the Food and Drug Inspection Station, Baltimore, Md., stated in correspondence that his chemists had found the modified Gutzeit method very satisfactory and had rarely experienced any trouble in obtaining duplicate determinations of arsenic in ordinary examination of food products. Hydrochloric acid is considered more satisfactory than sulfuric acid, but the use of both of these acids is allowed, the preference for hydrochloric acid being due, it was stated, to the fact that it gives a sharper line on the standard paper and is, therefore, easier to read accurately.

#### COMMENTS OF COLLABORATORS.

*Raymond Hertwig.*—The modified Gutzeit method seems to be sufficiently satisfactory to be adopted as an official method.

*H. Johnson.*—The only objection we have to the modified Gutzeit method is that it is long, and that it takes a good deal of care in order to produce satisfactory results. The only modification of this process we might suggest at present is to displace the arsenic in the final operation by the electrolytic decomposition of water instead of using zinc. With zinc the reaction is not always uniform, with the result that the dispersion of the stain is variable. With electrolytic action it might be possible to get a more uniform dispersion of the stain.

*E. H. Berry.*—The substitution of hydrochloric acid for sulfuric acid has proved entirely satisfactory. In fact in most cases it is preferable to sulfuric acid. I would certainly advise that the method be revised to allow the use of both acids.

#### DISCUSSION OF RESULTS.

The analytical results submitted by the collaborators are on the whole exceedingly satisfactory. Some slight digression is noted in the report on Erythrosine B and, judging from the tabulated results, the differences observed would seem to be due to a non-uniform sample. It may also be mentioned that this substance forms a residue insoluble in water following treatment with nitric acid, and that there is a possibility of iodine being carried over to the generation stage of the determination. Results on the other four samples, with the exception of two by the same collaborator, do not vary more than 0.3 of a micromilligram of arsenic trioxide, a satisfactory confirmation of the accuracy of the Gutzeit method in analyses of complex organic substances.

#### REPORT OF OUTSIDE WORK.

Cribier<sup>1</sup>, following an extensive investigation, announced that immediate immersion of the stained mercury-impregnated paper in 0.1N potassium iodide solution not only fixes the stain, but also produces a color change which tends to increase the sensitivity of the method. After treatment with the iodide solution and subsequent washing and drying, the stability of the stain is markedly increased, becoming quite resistant under such treatment to the action of light and moisture. It is of importance to note that this treatment gives a uniform, dark brown color to the arsenic complex, while it is apparently without effect on the similar antimony or phosphorus stains occasionally encountered in arsenic determinations.

The Purdue University Agricultural Experiment Station<sup>2</sup> has published results of an investigation showing the effects of arsenical sprays upon the mortality of bees. The fatal dose of arsenic for a bee was

<sup>1</sup> *J. pharm. chim.*, 1921, 24: 241.

<sup>2</sup> *Indiana Agr. Expt. Sta. Bull.* 247: 1921.

found to be somewhat less than 0.5 of a micromilligram of arsenic trioxide, and the investigation showed that the Gutzeit method is sensitive enough to determine most fatal doses.

The question of arsenic-sprayed apples and pears and also of celery contaminated by arsenic spray has received some study in the Western stations of the Bureau of Chemistry. It is expected that cooperation of the shippers and growers will decrease any possible menace from this source to a minimum.

#### CONCLUSION.

The present report has, to some extent, reviewed the work of the previous referee in an effort to summarize finally the results of the repeated collaborative study of the Gutzeit method. In addition, the potassium iodide reduction has been established as an essential step in the procedure. It has also been pointed out that hydrochloric acid is now so generally employed that its use should be authorized in the methods of the association.

Previous referees have remarked upon the value of the adoption as official by this association of the essential details of the Gutzeit method. Treuthardt<sup>1</sup> states: "Each analyst will by practice attain a uniformity in procedure which enables him to get consistent results". This assumption was also supported by Collins<sup>2</sup>, who suggested leaving the minor details to the discretion and convenience of the individual analysts. The present modified Gutzeit method is essentially that used by Smith. Later his conclusions were fully confirmed by Beck and Merres<sup>3</sup>, who recommended the method for the examination of articles of nutrition.

It is concluded, therefore, that since satisfactory results have been obtained by collaborative work and the modified Gutzeit method has been proved reliable by a number of independent workers, it should be accepted as official by the association.

#### RECOMMENDATIONS.

It is recommended—

(1) That the use of hydrochloric acid be allowed as an alternative acid in the Gutzeit method, and that the method as described<sup>4</sup> be revised as follows:

Following 1 (b) add "or hydrochloric acid, arsenic free (1 to 1)".

Following "and add 20 cc. of dilute sulphuric acid" page 148, add "or 20 cc. of 1 to 1 arsenic-free hydrochloric acid".

(2) That the Gutzeit method for the determination of arsenic, with the above revision and amendment, be adopted as an official method by this organization.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1917, 3: 43.

<sup>2</sup> *Ibid.*, 1921, 4: 454.

<sup>3</sup> *Arb. Kais. Gesundh.*, 1915, 50: 38.

<sup>4</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 147.

## CONTRIBUTED PAPERS.

STANDARDS OF ATTEMPTED SEPARATION, BY THE  
PERMANGANATE METHODS, OF THE BETTER  
AND THE POORER QUALITY OF INSOLUBLE  
FERTILIZER-NITROGEN<sup>1</sup>.

By BURT L. HARTWELL AND F. R. PEMBER (Agricultural Experiment  
Station, Kingston, R. I.).

Among the methods of the A. O. A. C.<sup>2</sup> are two official methods for determining the *active* water-insoluble nitrogen of fertilizers; one is frequently called the neutral and the other, the alkaline permanganate method. It has not been officially claimed, nor should it be claimed, that availability is determined by either one of the methods. The term "availability" conveys the conception that reference is made to the percentage available to crops; whereas, as has been stated, these methods for determining activity are incapable of furnishing definite information concerning availability. They simply attempt to separate, by the acceptance of arbitrary standards, not the good from the poor, but the better from the poorer quality of insoluble nitrogen, and it is not known that their authors make any greater claims for them.

The word "activity" is suitably indefinite. It, instead of "availability", should always be used when referring to the chemical methods, and should be accompanied by the name of the particular method employed. Fifty per cent activity, for example, by the alkaline method, should never be interpreted to mean that half of the insoluble nitrogen is as available to the crops as that in nitrate of soda; yet many people still persist in making such an interpretation. It is more probable that less than a quarter of it is available. Fifty per cent activity is sometimes considered as the dividing point between better and poorer quality, but it should not be assumed that material registering 70 per cent activity is necessarily any more available than material with an activity of 60 per cent. It simply means that a larger proportion of its nitrogen was distilled from the alkaline permanganate solution, and that both may be included in the better group.

During the past decade the Rhode Island station has been making comparisons between the availability of the insoluble nitrogen contained in considerable quantities in a given number of fertilizers (147 samples) as measured by the growth of oats or millet in 8-inch Wagner pots, and the activity as measured by the alkaline permanganate (147 samples),

<sup>1</sup> Contribution 298 of the Agricultural Experiment Station of the Rhode Island State College.

<sup>2</sup> *Assoc. Official Agr. Chemists, Methods*, 1920.

and also, in the majority of cases by the neutral permanganate methods (81 samples). Some of the earlier work<sup>1</sup> has been reported in detail by the authors, but a condensed statement of all samples is included in the accompanying compilation as a possible basis for adopting a standard for each method, which shall arbitrarily divide the insoluble nitrogen of fertilizers into better and poorer quality.

The availability of nitrate nitrogen has been placed at 100 in the statement, or of nitrogen in blood or hoof meal at 70, depending on which was accepted as a standard for comparison. The fertilizers are arranged in an increasing series according to the percentage availability by vegetation tests. These percentages are always accompanied by the per cent of the insoluble nitrogen which was distilled from alkaline permanganate (alkaline method) and in a majority of cases also by the per cent soluble in neutral permanganate (neutral method).

Availability	Activity		Availability	Activity		Availability	Activity		Availability	Activity		Availability	Activity		Availability	Activity		Availability	Activity	
	Alk.	Neut.		Alk.	Neut.		Alk.	Neut.		Alk.	Neut.		Alk.	Neut.		Alk.	Neut.		Alk.	Neut.
0	31	..	18	53	82	30	55	78	37	55	88	43	67	80	53	49	..	66	70	86
0	34	..	19	51	81	31	53	..	37	59	78	43	48	..	53	55	86	68	76	..
0	46	..	19	55	63	31	55	89	38	57	..	43	45	..	53	58	88	69	57	..
0	48	69	20	46	71	32	55	81	38	59	..	44	54	76	54	61	..	70	74	..
3	28	67	21	60	77	32	70	89	38	56	79	44	51	71	54	60	81	71	74	..
6	53	59	22	52	..	32	66	..	38	54	..	44	72	92	54	61	76	71	55	..
6	60	79	22	54	..	33	53	84	39	46	..	44	59	81	54	59	83	72	54	..
7	58	70	22	54	77	33	67	78	39	56	..	45	50	..	56	69	86	73	71	93
8	44	74	23	49	70	34	50	74	39	42	70	46	61	74	57	73	..	73	83	..
8	45	55	23	50	65	34	61	68	40	50	..	48	65	88	58	57	..	73	59	..
9	40	74	24	50	..	34	65	83	41	66	83	48	67	81	59	63	86	73	52	..
10	50	73	25	70	87	34	34	64	41	63	89	49	52	90	60	64	85	74	55	..
12	48	77	25	59	79	35	48	89	41	63	89	50	51	78	60	71	92	74	81	..
12	48	..	26	53	75	35	51	..	41	50	78	50	58	83	61	62	81	74	60	86
13	45	..	27	61	..	35	49	..	41	59	..	51	59	..	61	50	..	75	59	..
16	51	..	27	54	82	35	51	..	41	64	84	51	48	..	61	55	80	76	56	..
16	52	..	27	50	81	36	60	90	41	41	66	52	56	..	63	57	..	76	64	..
16	53	79	28	63	68	36	56	76	42	68	80	52	68	89	63	77	90	78	83	..
17	52	82	29	54	..	36	65	83	42	69	..	52	63	..	65	60	75	78	78	..
17	58	77	29	66	..	36	59	..	42	52	..	52	75	..	65	62	..	79	55	..
18	52	..	30	44	..	37	50	81	42	48	..	53	70	..	66	76	..	80	76	..

It is proposed for consideration that the poorer quality of insoluble nitrogen be that with an activity of less than 55 by the alkaline method, or less than 80 by the neutral method.

According to this standard for the alkaline method there were only four cases (11 per cent) in which the insoluble nitrogen would be considered of poorer quality by having an activity of less than 55, and yet have an actual *availability* of over 55. If this is considered unjust by the fertilizer manufacturer, he should notice that by the same standard there were eight cases (21 per cent) in which activity indicated a better

quality, whereas the insoluble nitrogen was not half as available, or had an availability of less than 28 per cent.

Of the samples having an availability of above 55, only ten activities were determined by the *neutral* method, one of which (10 per cent) had an activity of only 75. On the other hand, of the samples which were so poor as to have an availability of less than 28, twenty-six activities were determined by the neutral method, of which six (23 per cent) were indicated as being of the better quality by having an activity of over 80.

According to these proposed activity standards there were twice as many failures to condemn insoluble nitrogen so poor as to have an availability of less than 28, as there were failures to give credit to insoluble nitrogen which was twice as available. When both laboratory methods were used not a sample of insoluble nitrogen with an availability of over 55 was condemned by both methods; and in only one case did both methods fail to condemn samples showing an availability of less than 28. Samples having availabilities between 28 and 54 would be considered in twenty-four cases as of better quality by both activity methods, and in eight cases as of poorer quality.

There are strong arguments in favor of making determinations of activity by both methods in important cases.

## EXPERIMENTAL DATA ON PECTIN-SUGAR-ACID GELS.

By R. SUCHARIPA (Bureau of Agriculture, Prague, Czecho-slovakia).

It is a known fact that a jelly will form in a pectin solution only where a certain content of sugar and acid is present. The literature available on this subject, a list of which is given at the end of this paper, is not unanimous on either of these constituents, as regards concentration, the most varying figures being those given pectin. The discrepancies, no doubt, are caused by the fact that the constitution and the qualities of pectin differ with its origin and the way it is prepared. Besides, the notion of a jelly is an individual one; a certain product may be called good by some persons and soft by others. Several other factors which enter into the question, as time and temperature of setting, method of preparation, etc., have an influence on the strength of the jelly.

The purpose of this investigation was to show the importance of some of these conditions.

In the experiments the jellies were prepared from a solution containing 75 per cent of sucrose and 0.75 per cent of citric acid. If one-third in weight of a given amount of this sirup was added to a pectin solution, the whole resulted in a final concentration of 50 per cent of sucrose, 0.50 per cent of citric acid, and an amount of pectin which depended upon the strength of the pectin solution used. Thus, if to 15 grams of



sugar-acid sirup, 5 grams of a 4 per cent pectin solution were added, the whole formed a gel that contained 1 per cent of pectin in the final product. In this way it was possible to insure the exact proportion without boiling or concentrating the liquid, which necessarily would have changed both the sugar and the pectin, owing to the acid contained in the solution.

Mixtures prepared in this way formed a gel without any heating, if the required amount of pectin was present and the whole was allowed to stand for a certain time, at not too high a temperature.

That previous heating would not have an influence upon gel formation was made evident from the following experiment: Two sets of four Erlenmeyer flasks were filled with the same amount of a pectin-sugar-acid liquid as described above. One bottle was left open; the second was stoppered; the third was stoppered and heated in a water bath to 50°C. for half an hour; and the fourth was heated for the same time to 100°C. One set of bottles was left on the laboratory desk at a temperature of about 24°C., whereas the other four bottles, filled and treated in the same way, were put into an ice box. All the bottles were inspected daily. After four days the bottles kept in the ice box appeared more firmly set than those kept on the laboratory table. Scarcely any difference could be noticed between the contents of the heated bottles and the other bottles. The open bottles, however, showed a distinctly firmer gel, particularly the one from the laboratory desk.

It may be concluded, therefore, that heating the jelly liquid does not hasten setting. The gel forms more quickly at a low temperature, and *evaporation* promotes considerably the formation and the strengthening of a pectin-sugar-acid gel. Since evaporation was greater on the laboratory desk than in the ice box, the evidence for this fact was strengthened.

No attempt was made to follow these experiments quantitatively owing to lack of time.

That a gel may be obtained from a cold prepared mixture; that heat does not hasten the "reaction"; and that low temperatures and evaporation promote the setting to a gel pointed to no chemical reaction at all, as such reactions usually take place more readily at higher temperatures and are not favored by evaporation to such an extent. Gel formation seemed, therefore, to depend merely on concentration of the ingredients. This was made clear by a series of investigations and later by an interesting work of Mr. Lal Singh<sup>1</sup>. Its colloidal nature leads to the conclusion that the gel texture must be formed by the pectin component which becomes insoluble in the liquid phase, composed of sucrose, water, and acid, and gradually "crystallizes" out, or coagulates.

To afford more evidence for this supposition the following tests were

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<sup>1</sup> *J. Ind. Eng. Chem.*, 1922, 14: 710.

carried out: The sucrose-citric acid solution was overlaid with a pectin solution, care being taken not to mix the liquids. The test tube was stoppered to exclude the effect of evaporation, and after a few days the pectin layer could be removed in a coagulated solid state. A similar sucrose-acid liquid was poured over dry, powdered pectin and allowed to stand for an extended period of time. No pectin dissolved.

The pectin-sucrose-acid gel seems, therefore, to result from the coagulation of pectin in the remaining liquid phase, in which it is insoluble. This result receives further corroboration by the common phenomenon which is usually called "weeping" of jellies, caused by the mother liquor oozing out of the network of the pectin coagulum. If the meshes or honey-comb-like cells are small and dense, the capillary forces will retain the mother liquor within. If the network is coarse the sucrose-acid liquor will ooze out easily. The density of the gel, as well as the "weeping", evidently depends upon the pectin concentration.

A gel which contained 2 per cent of pectin gave about 15 per cent of oozed-out liquor, whereas a similar gel with only 0.75 per cent of pectin gave more than 60 per cent. In both cases the same pectin was used. The strong jelly, however, had to be centrifuged to yield the mother liquor, whereas the weak jelly was put on a filter, and the liquid allowed to ooze out gradually.

Both the liquid and solid phases were analyzed; the results fully confirmed the conclusions reached in the previous experiments. To free the solid phase of the mother liquor completely, it was washed in 75 per cent alcohol: the alcohol was gathered and after evaporation it was added to the oozed-out liquid phase.

The solid part of the gel, thus purified, contained pectin only; sugar and acid were present in such small quantities that an opinion that the solid part of the gel might be a sucrose-pectin-acid compound was not justified. It is very difficult to wash coagulums, and the small amounts of sugar and acid found were merely impurities. The pectin secured after dissolving and reprecipitating was probably left intact, for it yielded a perfect gel again when dissolved in the proportion of one per cent in a sucrose-acid sirup, as was done before.

The liquid part separated from the gel showed an interesting feature. Besides all the acid and sugar of the original jelly, it showed traces of pectin—not more important, however, than the impurities left in the solid part—and a certain amount of *methyl* alcohol. The latter could have resulted only by the partial decomposition of pectin, of which it forms a part. That such hydrolysis might take place due to the influence of the acid should not surprise, although it probably occurred only to a very small extent. Had the methoxyl groups been split off to any considerable amount, it would not have been possible to prepare a jelly again out of the pectin recovered from the solid phase.

If the jelly be boiled, though, for an extended period of time, the high temperature—above  $104^{\circ}\text{C}$ .—and the acid may affect the pectin seriously, and so destroy its coagulating properties. This is known in practice as “overcooking” a jelly, and may be the result of a loss in the methoxyl groups of the pectin or some other change, as will be shown later.

From an earlier investigation carried out during 1921–1922 in the Chemical Institution of the Charles University in Prague, Czechoslovakia, it appears that the cell wall in plant tissues contains a range of pectins from almost 12 per cent to practically 0 per cent methoxyl content. Using different methods of extraction, pectins with varying amounts of methoxyl could be obtained, which probably represented groups of pectins. The proportion of methyl alcohol found by estimation no doubt represented the average content of the group.

It was to be expected that such pectins would behave differently in their gel-forming properties, and as a support to this view the well-known fact may be cited that pectin deprived of all its methoxyl groups, *i. e.*, pectic acid, does not form any gel at all.

To secure the purest possible pectins, the white part, or albedo, of lemons was used as raw material. After being run through a meat grinder it was cooked out several times in alcohol with a reflux condenser, until the alcohol remained colorless, and then was air dried. The resins, tannins, terpenes, and glucosides being thus removed, the first pectin extraction was made with *cold* water. This yielded a fully methoxylated pectin, and since this could be extracted with cold distilled water, it must exist in a free state in the tissue. It is called free pectin.

The next extraction was made in an autoclave under one to one and a half pounds pressure, boiling being continued for 40 minutes. This may be repeated under the same conditions, and a third pectin will result.

To secure a wider range of pectins, the pulp of the lemons was also used. It was ground, washed for several hours in flowing tap water until free from acids and sugars, then washed with distilled water, and finally extracted under steam pressure, as above—the first extraction being exactly one pound pressure for half an hour, and the second two pounds for one hour.

In order to see what effect prolonged heating under higher pressure would have upon the gel-forming properties, the second extraction in the autoclave made from the peel albedo was heated for one and a half hours under three pounds pressure.

Five differently prepared pectins were obtained: (1) Free pectin from albedo, extracted with cold water; (2) pressure pectin, one-half atmosphere for half an hour, from pulp; (3) pressure pectin, three-fourths atmosphere, for 40 minutes, from albedo; (4) pressure pectin, one atmos-

phere, for 60 minutes, from pulp; and (5) pressure pectin, one and one-half atmosphere for 90 minutes, from albedo.

After filtration, the liquids were precipitated with alcohol, then re-dissolved in distilled water, and precipitated again with alcohol containing a few cc. of hydrochloric acid, as is usually done. Four such reprecipitations were made with each pectin, samples of No. 1 and No. 2 pectins being kept crude too, in order to see whether by purification some component aiding jellification had not been lost.

The pectins were washed finally with alcohol containing some sodium chloride, then with pure alcohol until no chloride was present, finally with ether, and then dried under vacuum at 100°C. Having attained constant weight, they were analyzed for their ash and methoxyl content, Zeisel's method being used for the latter estimation. The following results were obtained:

		ASH	METHOXYL, CH <sub>3</sub> O
		<i>per cent</i>	<i>per cent</i>
No. 1	Free pectin, crude . . . . .	5.04	9.40
	Free pectin, purified . . . .	0.43	12.32
No. 2	Pressure pectin, crude . . .	1.96	8.90
	Pressure pectin, purified . .	0.19	11.49
No. 3	Pressure pectin, purified . .	0.25	11.33
No. 4	Pressure pectin, purified . .	0.27	10.43
No. 5	Pressure pectin, purified . .	0.59	10.55

The decreasing amount of methoxyl groups is quite evident. In the purified pectins it declines from 12.32 per cent in No. 1 to 10.43 per cent in No. 4. The amount of methoxyl in No. 5, which is slightly higher, probably originates from hemicelluloses which have been loosened along with the pectin during the long heating at a higher pressure. The last pectin can not be considered as quite pure.

The figures for No. 1 and No. 2, purified and not purified, show that besides mineral impurities there must be a considerable amount of organic impurities too, for the methoxyl content in the crude pectins is about one-third lower than that of the purified ones, whereas the ash contents amount only to 5.04 and 1.96 per cent, respectively.

The high rate of ash in No. 1 shows that the main part of the mineral salts is probably removed by the first water extraction.

When dissolved in water, these pectins showed a very marked difference in character. The viscosity of their solutions decreased considerably with their methoxyl content. Thus it was nearly impossible to obtain a 10 per cent solution of No. 1, whereas from No. 4 and No. 5 even more concentrated solutions could be prepared.

Even the alcohol precipitates were different, the last pectins showing a more pasty consistency than the first ones.

In order to test the gel properties of these pectins, two methods were resorted to.

In the first method jellies were prepared as previously described, starting with a concentration of pectin of 0.25 per cent and increasing the pectin content until each of the pectins just caused the liquid to jell. The quantities of sucrose-acid sirup and pectin necessary were weighed into the beakers, which were kept in the ice box for 24 hours and then examined, the beakers being inclined so as to make the contents flow. When the gel separated from the glass wall and retained its shape, it was considered a satisfactory gel.

After such a "minimum" concentration for the various pectins had been established, a range of gels was prepared, the minimum quantity found for each pectin being used. The jellies obtained in this way presented, after a slight correction and a new test, an absolutely equal consistency. The following corresponding minimal quantities of pectin in the final gel, expressed as per cent, were established:

	No. 1	No. 2	No. 3	No. 4	No. 5
Crude.....	0.44	0.88	....	....	....
Purified.....	0.35	0.70	0.75	0.90	4.0

The increasing amount of pectin necessary to produce a jelly, with its decreasing content of methoxyl groups, is distinctly shown. The jump from 0.90 per cent with No. 4, to 4.0 per cent with No. 5 proves how deleterious long heating and high temperatures may be to pectins. It also shows that it is not the methoxyl group alone which gives gel properties to pectins, for No. 4 and No. 5 had very nearly the same methoxyl content. In No. 5, however, the methoxyls may not belong to pectins, as there must have been a certain content of hemicelluloses in this pectin. Therefore it is only the methoxyl content of the pectin itself which may be considered as valuable for gel properties. The relation between purified and non-purified pectins is equally interesting. It was shown that the crude pectins contained about 30 per cent less methoxyl than the corresponding purified ones. This may lead to the conclusion that there was 30 per cent of impurities or of some easily split off component. Whatever it is, this additional matter has decidedly no gel-forming or gel-promoting properties, since it was necessary to increase the amount of crude pectins by about 25 per cent to obtain the same strength of jelly as from the purified ones. The amount of pectin necessary to form a jelly, therefore, largely depends upon its purity, upon its methoxyl content, and upon the method by which it is prepared.

These results will give some explanation of the widely differing figures which have been obtained by the various jelly investigators.

In the second method a scheme was devised for the dynamical test of the gels. From the accompanying sketch (Fig. 1) it will be seen that it consists of a glass tube on the lower end of which a metallic capsule was cemented, having a hole of about 1 cm. diameter. A thin jelly

layer was produced on the bottom of the capsule by pouring in a certain amount of jelly liquid; in this case it was 3 cc. each time. Care must be taken to close the hole. This is best done by putting the tube on a flat rubber stopper of the same diameter and joining the tube and stopper by slipping a large piece of rubber tube over them. The surface of the stopper must be slightly rubbed with vaseline to prevent the jelly from sticking to it. When removing the stopper, after the gel has formed, it must be carefully slipped off, as the jelly will break otherwise. The gel must be prepared from rather concentrated pectin solutions—those

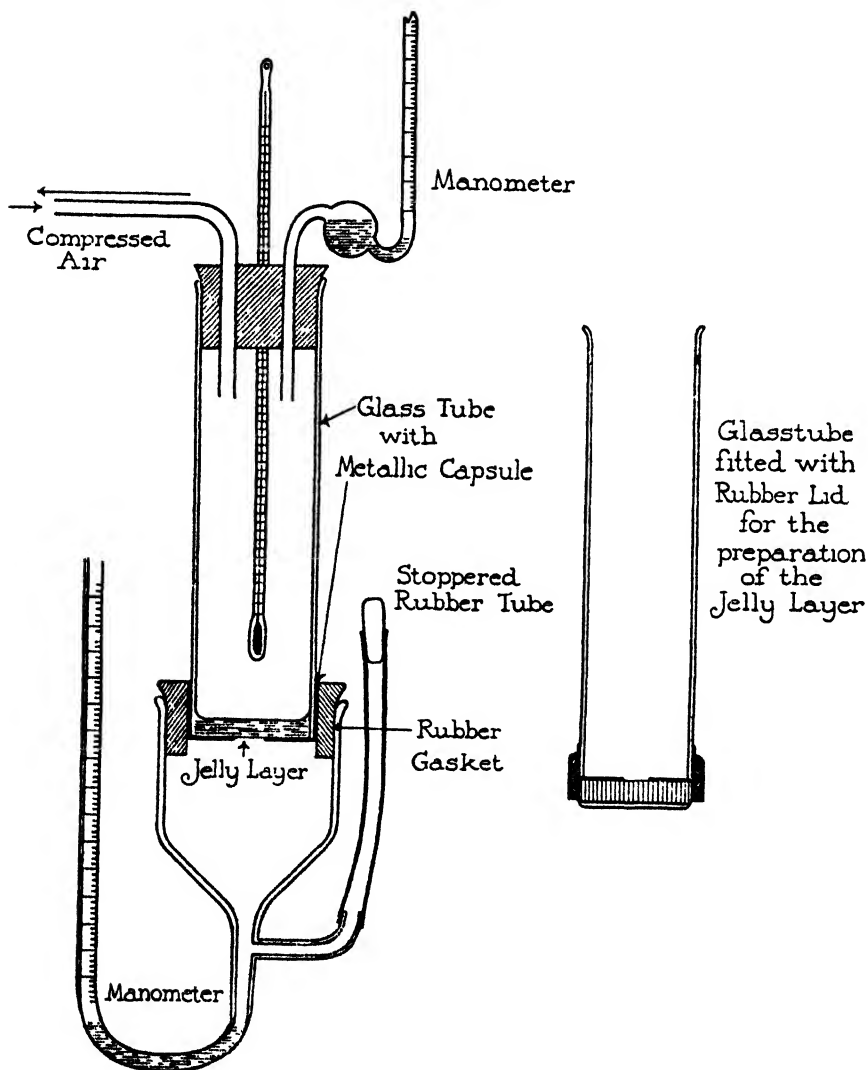


FIG. 1—GEL TESTER.

which contain at least  $1\frac{1}{2}$  per cent of the best pectin—and care must be taken to maintain the identical conditions, especially as regards quantity, in order to produce a layer of equal thickness, and also as regards time of setting and temperature.

The tube is provided with a stopper bearing a thermometer, a water manometer (open), and a glass tube connected with compressed air. In order to insure a uniform temperature at time of testing the capsule of the tube is fitted into a glass container by means of a rubber gasket, and the whole may be plunged into a water bath of a certain temperature. The second glass container may also bear a manometer and a stop-cock which is closed only after the upper tube has been fitted in, as otherwise the compression of air would result in an undesirable pressure in the lower container.

The measuring is very simple. After the thermometer shows the temperature desired—in this case it was always  $10^{\circ}\text{C}$ .—a very gentle air pressure may be imposed on the gel layer. The air current from a pump is best regulated by a cylinder filled with mercury into which a branch of the air tubing is dipped. Any air having more than the desired pressure will escape. Higher pressures are obtained by slowly dipping this branch deeper into the mercury.

The jelly layer will pouch out through the hole in the middle of the capsule, and after the pressure has attained a certain degree, which may be read on the manometer, it will break. The climax is followed by a sudden drop of the manometer, and, if colored water has been used, the glass tube of the manometer will show exactly how high the liquid rose. Gels may show not only different firmness but also different elasticity. To compare this property the second manometer in the lower container may be used, for it indicates only the volume of air taken by the pouched-out gel layer. The more it will pouch out, the higher the elasticity. In the present experiment only the pressures which the jellies would stand were measured. Two per cent pectin content was used for all the jellies except No. 5, where four per cent had to be used. After 24 hours in the ice box, the measurements were made as shown previously.

Although the principle of this method is very simple it requires some skill to obtain reliable results. Several tubes of the same width and provided with absolutely the same size of capsules may be used, but it will be necessary to calibrate them, *i. e.*, make several measurings for the same gel, in every tube, to see whether results are absolutely uniform.

The highest pressures that the gels of the various pectins could stand, expressed in centimeters of water, are as follows:

	No. 1	No. 2	No. 3	No. 4	No. 5
Crude pectin (2 per cent contained in gel)	31.5	27.5	....	....	....
Purified pectin (2 per cent contained in gel)	33.0	29.0	28.0	26.0	6.0

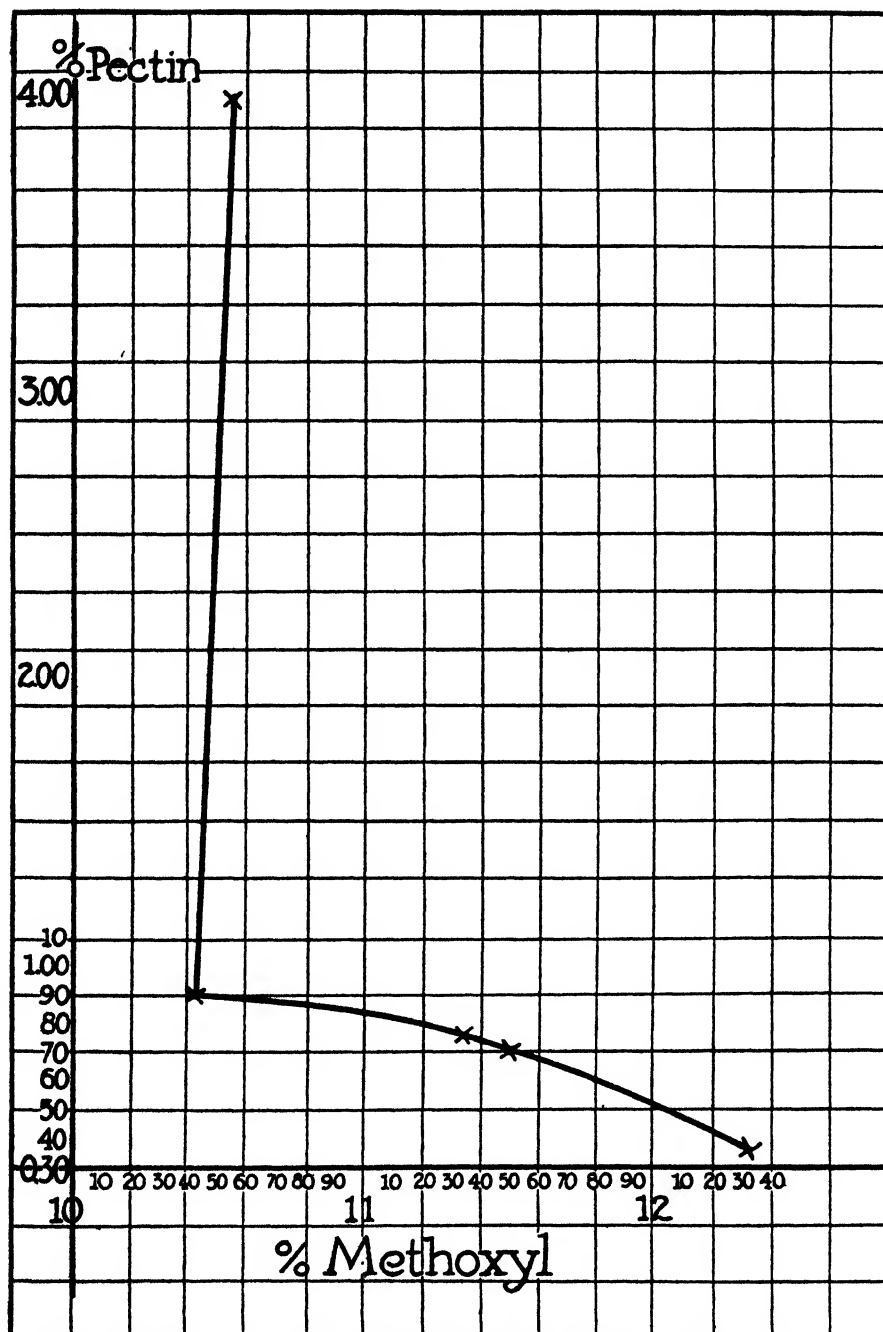


FIG. 2—DIAGRAM SHOWING RELATION BETWEEN SMALLEST QUANTITY OF PECTIN NECESSARY TO PRODUCE A GEL, AND THE METHOXYL CONTENT OF PECTIN USED.



The pressure for No. 5, 6.0 cm., is given for a pectin concentration of 4.0 per cent.

The results obtained by the "minima" and the dynamical methods are expressed by curves, and compare fairly well, as may be seen.

There is one peculiarity about the different jellies that is of interest in culinary science. Their taste is quite different. The free pectin and also No. 2 and No. 3, which are the first steam-extracted pectins, give jellies of the ordinary taste found in good fruit jellies, whereas No. 4 and still more, No. 5, give jellies with a gummy taste and of a sticky character.

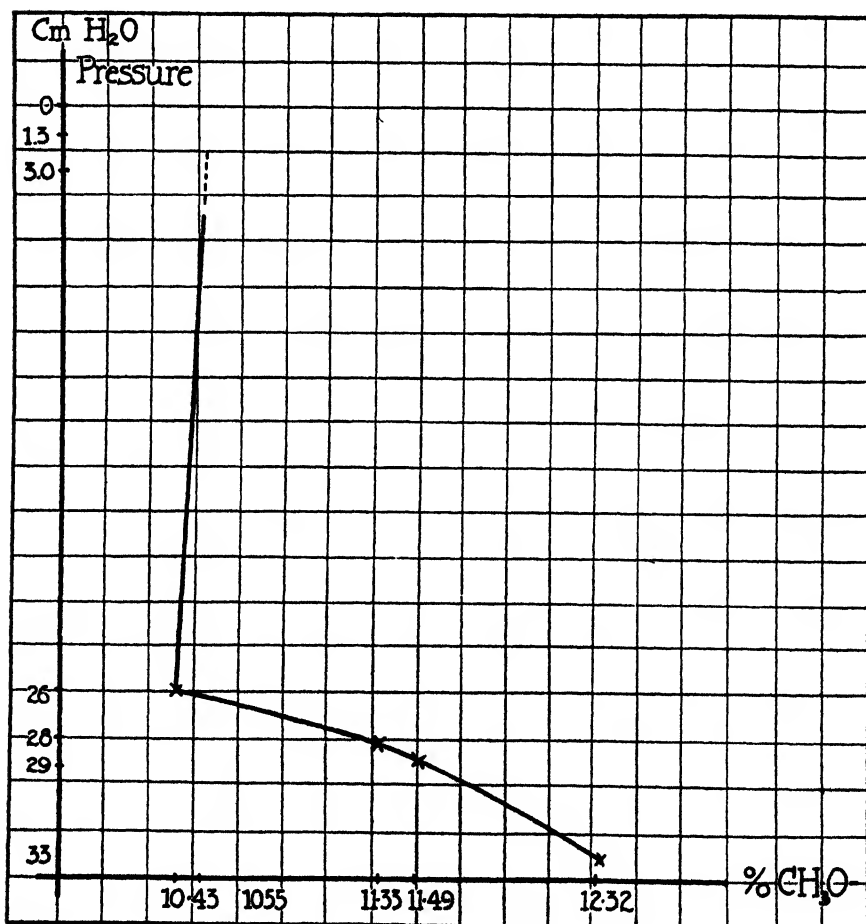


FIG. 3—AIR PRESSURE DIAGRAM.

Showing relation between strength of Jelly Films from different Pectins and their METHOXYL CONTENT.

For Pectin No. 5 the pressure of 6 cm. has been reported as 3 cm. only, since its concentration was twice as high as that of the other pectins.

It will be necessary to complete this investigation in several respects, namely, the exact determination of the solubility of pectin in sugar and in sugar-acid solutions, the effect of strengthening of jellies by evaporation, and the content of the liquid phase in jellies of different strength. The last may prove a good means of determining the strength of jellies.

#### SUMMARY.

- (1) Pectin-sucrose-acid gels may be prepared in a cold way.
- (2) Heat does not hasten the setting of such gels.
- (3) Low temperatures and evaporation are strong promoting factors.
- (4) The formation of such gels is not a chemical reaction. It is the coagulation of pectin in the liquid sucrose-acid medium.
- (5) Pectin is very slightly soluble in sucrose-acid solutions of certain concentration.
- (6) The mother liquor separates even out of very tough jellies, though in a smaller amount than out of soft jellies.
- (7) The solid part left contains pectin only (after washing in alcohol).
- (8) The liquid part contains all the acid, sugar, traces of pectin, and a small amount of *methyl alcohol*.
- (9) The methoxyl groups are split off in a small amount only, since the recovered pectin forms good gels again with sugar and acid.
- (10) Pectins with different methoxyl contents were prepared.
- (11) Crude pectins differ from purified pectins not only by their ash content, but also by some organic compounds.
- (12) The differently methoxylated pectins form solutions of uneven viscosity.
- (13) Two methods are described to compare gel-forming properties of various pectins. A device is described to serve as a gel-tester.
- (14) Pectins will form gels increasing in strength with their increasing methoxyl content. Impurities in pectins have no effect on gel strength providing the same amount of pectin is used.
- (15) Long heating and high temperature and pressure destroy jell power in pectins.

#### ACKNOWLEDGMENT.

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## COMPOSITION OF COMMERCIAL MUSTARD SEEDS AND THE DETECTION OF ADDED MUSTARD BRAN IN PREPARED MUSTARD.

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San Francisco, Calif.).

The practice of substituting more or less mustard bran for mustard seed in prepared mustard is rather common. Certain prepared mustards, known to contain added mustard bran, have been found to fall within the 12 per cent limit for crude fiber in the fat- and salt-free solids, as defined by the U. S. Department of Agriculture standard for prepared mustard<sup>2</sup>, when analyzed by the modified method for crude fiber determination<sup>3</sup> recommended for adoption by the A. O. A. C. in 1921. The

<sup>1</sup> The writer wishes to acknowledge the criticism of this manuscript by R. W. Hiltz, Chief, Food and Drug Inspection, Western District. T. O. Kellems, Analyst, San Francisco Station, assisted in the analyses.

<sup>2</sup> U. S. Dept. Agr. Circ. 136, Office of the Secretary.

<sup>3</sup> J. Assoc. Official Agr. Chemists, 1922, 6: 94.

standard therefore appeared too liberal. For this reason a systematic analysis was undertaken of all the varieties of mustard seed now used commercially.

Three distinct objects were in view: (1) To determine the general composition and in particular the crude fiber content of commercial mustard seeds as used at present by manufacturers of prepared mustard; (2) to ascertain whether the proposed modified method for the determination of crude fiber in prepared mustard gives results which are comparable to the crude fiber content of the original seed used in the manufacture of the product; and (3) to develop any additional means of detecting small proportions of added mustard bran in prepared mustard.

Samples of commercial mustard seed were obtained, representing as many of the chief mustard-producing regions of the world as possible. These were obtained from manufacturers of prepared mustard, spice dealers and from importations at ports of entry, collected at New York, San Francisco, Seattle, Denver, and Los Angeles.

#### PREPARATION OF SAMPLES FOR ANALYSIS.

The seeds were prepared for analysis by passing about 300 grams through a drug mill. Owing to the oily and gummy nature they had to be used in a coarse condition as they could not be put through the mill successfully a second time. No attempt was made to remove any sand which might be present, the analyses being made as the seeds were used in the factory.

#### METHODS OF ANALYSIS.

The methods found in "Official and Tentative Methods of Analysis, 1920 Edition", are the ones referred to in this paper unless otherwise indicated.

#### MOISTURE.

The tentative method for moisture in spices, XXIII, 2, requires 2 grams of sample to be dried to constant weight at 110°C. Comparative results by drying 2-gram samples in a water oven, an air oven, and a vacuum oven were tried on one sample, with the following results:

#### *Moisture.*

WATER OVEN 97°C.	AIR OVEN 110°C.	VACUUM OVEN 28 in.—96°C.
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
6.52	7.13	7.50
6.49	7.27	7.63

Since the vacuum oven method gave the highest results, it was used in these investigations.

## ASH AND RELATED DETERMINATIONS.

Total ash, water-insoluble ash, alkalinity of soluble and insoluble ash, acid-insoluble ash, and salt were all determined by the following official methods: XXIII, 3, 4, 5, 27 and VIII, 15, 16. The Volhard method for salt was used, II, 17.

## NITROGEN.

The official Gunning method (I, 21) was used for nitrogen. The digestions were continued 5 hours after clearing took place. The recommendations of Paul and Berry in their paper, "The Kjeldahl Nitrogen Method and its Modifications", were observed<sup>1</sup>.

## ETHER EXTRACT.

Since no volatile oil, as such, exists in mustard seed, the ether extract was determined by the official direct method for foods and feeding stuffs (VII, 10) with the modifications noted below, instead of the official method as described for spices. Two-gram samples were used. After 10 hours' extraction in a Knorr extractor the ether was allowed to evaporate from the sample. The dry residue was shaken into a mortar, the asbestos pad being left in the tube, and ground fine with the pestle; it was then returned to the tube and extracted for 6 hours additional. This was necessary owing to the impossibility of grinding the samples fine at the start. The effect of this regrinding is shown below:

ETHER EXTRACT		per cent
On coarsely ground sample. . . . .		34.60
		34.44
On same after regrinding and further extraction. . . . .		34.84
		34.85

## CRUDE FIBER.

The determination of crude fiber in mustard seed is largely influenced by the fineness of the sample. For example, it was found that crude fiber, as determined in a rather coarsely ground sample after previous extraction of the fat with ether, was 9.06 per cent, whereas the same sample showed only 6.11 per cent of crude fiber when the material was finely pulverized in a mortar after preliminary extraction of the fat with ether. Since mustard seed in the form of prepared mustard is ground very fine, it is necessary that the samples of mustard seed be ground fine before making the crude fiber determination; otherwise the figures obtained will be entirely useless in the interpretation of analyses of prepared mustard. Accordingly, in this work, the residues from the ether extract determinations, which had been ground fine in a mortar after

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 108.

the fat was partly extracted, were used for the crude fiber determination, the residue and the asbestos being transferred to the crude fiber flask. From this point the details of the method adopted as official (first reading) at the 1921 meeting of the A. O. A. C.<sup>1</sup> were strictly adhered to.

The effect of fineness of grinding on crude fiber determinations was clearly shown in another experiment. In one of the experimental lots of prepared mustard made in a factory and described later (Sample 50), crude fiber was determined on the coarsely ground product before it had received its final grinding on the stones. In this condition it showed 16.1 per cent of crude fiber in the fat- and salt-free solids. The same product, after final grinding, showed only 8.9 per cent crude fiber on the same basis. In both cases the fat was extracted from the material before the crude fiber determination had been made by the Hilts-Hertwig modification.

For determination of crude fiber in prepared mustard in this investigation the fat was first extracted by the procedure of Hilts and Hertwig as follows:

*Crude Fiber Method for Prepared Mustard.*

Weigh 10 grams of the sample and transfer to an 8-ounce nursing bottle with 50 cc. of strong alcohol, stopper, and shake vigorously. Add 40 cc. of ethyl ether, shake, and let stand about 5 minutes with occasional shaking. Centrifuge and decant off the alcohol-ether mixture. Treat twice more with 40 cc. portions of ether, shaking, centrifuging, and decanting as before. Rest the bottle on its side for a time to permit most of the ether to evaporate spontaneously. Transfer the material to a 750 cc. Erlenmeyer flask with 200 cc. of boiling 1.25 per cent sulfuric acid, add  $\frac{1}{2}$  to 1 gram of asbestos and proceed with the official crude fiber method<sup>1</sup>. If preferred the sample may be treated with the alcohol and ether in a small beaker, finally transferred to a hardened 11 cm. filter paper, and washed two or three times with ether. Permit to drain completely, but not to dry or cake, and proceed as above.

This method was recommended for adoption at the 1921 meeting of the A. O. A. C. by the Associate Referee on Spices and Other Condiments, but definite action was not taken by the association pending final action on the general method for crude fiber<sup>2</sup>. Comparison of crude fiber determinations by this method and by the previous tentative method (XXIII, 32) on a considerable number of samples showed definitely that this method gives more consistent and reliable results than the older one. The results are almost invariably lower. Clemens has described a method which is identical in principle and arrives at the same conclusion, i. e., that previous extraction of the fat gives lower and more consistent results<sup>3</sup>.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 421.

<sup>2</sup> *Ibid.*, 6: 94, 149.

<sup>3</sup> *Ibid.*, 205.

TABLE  
Composition of Yellow and  
(Averages of duplicate  
Yellow

SAMPLE NO.	ORIGIN OF SEED	ON ORIGINAL MATERIAL										
		Moisture Vacuum 100°C.	Ether Extract	Nitro- gen	Crude Fiber	Volatile Oil of Mustard	Total Ash	Water-insolu- ble ash	Acid-insolu- ble ash	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	England..	7.73	31.28	4.09	6.48	....	4.50	3.21	0.08	2.11	0.756	0.448
2	England..	7.17	31.46	4.11	6.54	0.06	5.05	4.29	0.17	2.07	0.786	0.480
3	England..	6.23	31.91	4.17	6.42	0.06	4.55	4.04	0.13	1.92	0.748	0.464
4	England..	6.71	29.78	4.49	6.62	0.05	4.45	3.90	0.06	2.02	0.732	0.500
5	California	7.22	27.72	4.83	6.30	0.06	4.51	3.82	0.00	1.91	0.668	0.436
6	California	7.08	27.91	5.43	5.40	0.06	3.57	3.01	0.02	1.62	0.521	0.417
7	California	7.22	29.38	4.40	6.21	0.06	4.98	4.19	0.03	2.47	0.723	0.598
8	California	7.15	27.77	5.22	5.69	0.04	3.80	3.30	0.03	1.68	0.604	0.430
9	California	7.17	27.52	5.13	5.82	0.06	3.80	2.73	0.07	1.78	0.531	0.512
10	California	8.21	27.23	5.10	5.52	0.05	4.66	4.08	0.03	2.06	0.554	0.579
11	California	7.11	27.57	5.24	5.28	0.06	3.72	2.73	0.07	1.51	0.494	0.435
12	California	7.41	27.50	5.25	5.36	0.05	3.68	2.82	0.04	1.50	0.478	0.401
13	California	8.71	26.01	5.18	5.34	...	3.68	3.12	0.09	1.56	0.535	0.445
14	California	7.07	29.28	4.58	6.07	0.06	5.23	4.44	0.10	2.32	0.723	0.626
15	California	7.28	28.62	4.45	5.94	0.05	5.05	4.32	0.05	2.41	0.615	0.608
16	California	8.22	29.50	4.56	5.57	....	5.47	4.66	0.12	2.57	0.755	0.542
17	Holland..	7.32	32.36	3.93	6.64	0.06	4.89	4.13	0.21	2.08	0.783	0.486
18	Denmark.	6.79	29.67	4.65	6.27	0.05	4.80	4.12	0.48	1.79	0.712	0.486
	Maximum	8.71	32.36	5.43	6.64	0.06	5.47	4.66	0.48	2.57	0.786	0.626
	Minimum	6.23	26.01	3.93	5.28	0.04	3.57	2.73	0.00	1.50	0.478	0.401

*Brown*

19	England..	7.37	29.48	4.42	6.31	1.17	5.39	3.58	0.30	2.37	0.794	0.536
20	England..	6.66	30.00	4.65	5.81	1.32	5.38	4.85	0.20	2.47	0.789	0.627
21	California	7.03	39.74	3.82	5.62	0.76	4.62	4.00	0.16	2.34	0.639	0.706
22	California	6.81	39.85	3.68	5.44	0.69	4.51	3.87	0.10	2.21	0.741	0.586
23	California	7.68	31.96	4.83	4.84	0.94	4.32	3.50	0.13	1.89	0.516	0.561
24	California	7.84	39.46	3.51	5.67	0.55	4.57	4.01	0.11	2.16	0.592	0.667
25	California	7.73	35.20	4.15	5.30	0.99	4.79	3.80	0.21	2.21	0.599	0.661
26	California	7.48	35.11	4.14	5.58	1.05	4.73	4.12	0.17	2.23	0.589	0.664
27	California	7.85	37.76	3.84	5.44	....	4.64	3.99	0.25	2.27	0.605	0.717
28	California	6.78	36.35	4.16	5.90	1.01	3.68	3.07	0.08	1.66	0.549	0.529
29	California	7.56	34.84	3.83	5.81	0.85	5.10	4.59	0.22	2.29	0.797	0.701
30	California	8.19	31.38	4.71	4.81	....	4.38	3.91	0.08	1.81	0.553	0.568
31	Italy.....	6.63	34.91	3.92	6.01	1.09	5.15	4.75	0.39	2.00	1.014	0.594
32	Chili.....	7.77	29.76	4.01	6.87	1.10	4.91	4.50	0.06	2.10	0.930	0.610
33	Unknown..	6.76	29.57	4.17	6.11	0.90	8.97	8.46	3.66	2.22	0.853	0.612
	Maximum	8.19	39.85	4.83	6.87	1.32	8.97	8.46	3.66	2.47	1.014	0.717
	Minimum	6.63	29.48	3.51	4.81	0.55	3.68	3.07	0.06	1.66	0.516	0.529

\*Alkalinity, water-soluble ash, 12 samples (cc. 0.1N acid per gram)—maximum 0.45 cc.; minimum, 0.10 cc.

†Alkalinity, water-insoluble ash, 12 samples (cc. 0.1N acid per gram)—maximum 4.00 cc.; minimum, 1.79 cc.

‡On moisture- and fat-free basis, except Sample 33, brown seed, which is on moisture-, fat-, and acid-insoluble ash-free basis.

§Chlorides in 9 samples—trace.

||Alkalinity, water-soluble ash, in 11 samples (cc. 0.1N acid per gram)—maximum, 0.60 cc.; minimum, 0.07 cc.

¶Alkalinity, water-insoluble ash, in 11 samples (cc. 0.1N acid per gram)—maximum, 4.01 cc.; minimum, 1.26 cc.

|||Moisture-, fat-, and acid-insoluble ash-free basis.

1.

*Brown Mustard Seed.\**

(determinations.)

*Mustard Seed.*

ON MOISTURE- AND FAT-FREE BASIS					RATIOS					
Nitrogen	Crude Fiber	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	N C. F.	P <sub>2</sub> O <sub>5</sub> C. F.	MgO C. F.	CaO MgO	(A) CaO×CF P <sub>2</sub> O <sub>5</sub> ×N	(B) At MgO
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>						
6.71	10.6	3.46	1.240	0.735	0.63	0.33	0.07	1.69	0.57	0.77
6.70	10.7	3.37	1.281	0.782	0.63	0.32	0.07	1.64	0.60	0.77
6.74	10.4	3.10	1.209	0.750	0.65	0.30	0.07	1.61	0.60	0.88
7.07	10.4	3.18	1.152	0.787	0.68	0.30	0.07	1.46	0.53	0.67
7.42	9.7	2.94	1.027	0.670	0.77	0.30	0.07	1.53	0.46	0.69
8.35	8.3	2.49	0.801	0.641	1.00	0.30	0.08	1.25	0.32	0.50
6.94	9.8	3.90	1.140	0.943	0.71	0.40	0.10	1.21	0.41	0.43
8.02	8.7	2.58	0.928	0.661	0.92	0.29	0.07	1.40	0.39	0.59
7.85	8.9	2.73	0.813	0.784	0.88	0.31	0.09	1.04	0.34	0.43
7.90	8.5	3.19	0.858	0.897	0.92	0.37	0.10	0.96	0.29	0.32
8.02	8.1	2.31	0.756	0.666	0.99	0.29	0.08	1.13	0.33	0.49
8.07	8.2	2.30	0.734	0.616	0.98	0.28	0.07	1.19	0.32	0.52
7.93	8.2	2.39	0.820	0.682	0.97	0.29	0.08	1.20	0.35	0.51
7.20	9.5	3.64	1.136	0.984	0.75	0.38	0.10	1.15	0.41	0.42
6.94	9.3	3.76	0.959	0.949	0.75	0.40	0.10	1.01	0.34	0.36
7.32	8.9	4.13	1.212	0.934	0.82	0.46	0.10	1.39	0.36	0.38
6.52	11.0	3.45	1.298	0.806	0.59	0.31	0.07	1.61	0.64	0.79
7.32	9.9	2.82	1.120	0.765	0.74	0.29	0.08	1.46	0.54	0.71
8.35	11.0	4.13	1.298	0.984	1.00	0.46	0.10	1.69	0.64	0.88
6.52	8.1	2.30	0.734	0.616	0.59	0.28	0.07	0.96	0.29	0.32

*Mustard Seed†.*

7.00	10.0	3.75	1.257	0.849	0.70	0.37	0.08	1.48	0.48	0.56
7.34	9.2	3.90	1.245	0.990	0.80	0.42	0.11	1.26	0.40	0.40
7.18	10.6	4.40	1.200	1.326	0.68	0.42	0.12	0.90	0.40	0.30
6.90	10.2	4.14	1.389	1.098	0.68	0.41	0.11	1.26	0.50	0.45
8.00	8.0	3.13	0.855	0.929	1.00	0.39	0.12	0.92	0.27	0.29
6.66	10.8	4.10	1.123	1.266	0.56	0.38	0.12	0.89	0.44	0.35
7.27	9.3	3.87	1.050	1.158	0.78	0.42	0.12	0.91	0.35	0.30
7.21	9.7	3.88	1.026	1.157	0.74	0.40	0.12	0.89	0.36	0.31
7.06	10.0	4.17	1.112	1.318	0.71	0.42	0.13	0.84	0.38	0.29
7.31	10.4	2.92	0.965	0.930	0.70	0.28	0.09	1.04	0.47	0.50
6.65	10.1	3.98	1.384	1.217	0.66	0.39	0.12	1.14	0.53	0.43
7.79	8.0	3.00	0.915	0.940	0.98	0.38	0.12	0.97	0.31	0.33
6.71	10.3	3.42	1.734	1.016	0.65	0.33	0.10	1.71	0.78	0.77
6.42	11.0	3.36	1.489	0.976	0.59	0.31	0.09	1.52	0.76	0.78
\$6.95	\$10.2	\$3.70	\$1.421	\$1.020	0.68	0.36	0.10	1.39	0.56	0.55
8.00	11.0	4.40	1.734	1.326	1.00	0.42	0.13	1.71	0.78	0.78
6.42	8.0	2.92	0.855	0.849	0.56	0.28	0.08	0.84	0.27	0.29



## TOTAL PHOSPHORIC ACID.

The total phosphoric acid was determined in the ash by the official volumetric method (I, 7, 8, 9). The addition of a saturated solution of calcium acetate to the samples before ashing was found necessary to get uniform and consistent results. It also gave considerably higher results.

Therefore, for the determination of total phosphoric acid, the samples were first moistened with 3 cc. of saturated calcium acetate solution, dried, and ashed at a low red heat. The final ash was treated with concentrated nitric acid, the solution heated on the steam bath 10 minutes, and then made up to some definite volume. It was found practicable to ash 3 grams, make up to 200 cc., and use 50 cc. for the determination.

## CALCIUM AND MAGNESIUM OXIDE.

The filtrate from the acid-insoluble ash was used for the determination of calcium and magnesium oxides. It was brought to dryness on the steam bath. The residue was heated for one-half hour, treated with dilute hydrochloric acid, heated again, the solution diluted to about 50 cc., and the silica filtered out. The calcium and magnesium were determined in the filtrate<sup>1</sup>.

## DISCUSSION OF DATA ON MUSTARD SEED.

Data on the analyses of 43 yellow, brown, and oriental mustard seed samples are given in the tables.

Certain ratios between the different constituents, so chosen as to differentiate between whole seed and bran, are included in the tables. The last two ratios, designated as A and B, are compound ratios defined as follows:

$$A = \frac{\text{CaO} \times \text{Crude Fiber}}{\text{P}_2\text{O}_5 \times N},$$

$$\text{and } B = \frac{A}{\text{MgO}}.$$

In ratio B the MgO is expressed on the fat- and salt-free solids basis, otherwise the ratio would not be comparable for mustard seed and prepared mustard. Ratio B involves all the different determinations which appear to differentiate whole seed from bran.

Attention is called to the uniformity of composition of all mustard seeds. This is most noticeable on the moisture- and fat-free basis, or moisture-, fat-, and acid-insoluble ash-free basis, where the acid-insoluble

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 300.

TABLE 2.  
Composition of Oriental Mustard Seed.\*  
(Averages of duplicate determinations.)

SAMPLE NO.	ORIGIN OF SEED	ON ORIGINAL MATERIAL										ON MOISTURE- AND FAT-FREE BASIS							
		Moisture vac. 100°C.		Ether extract	Nitro-gea	Crude Fiber	% Volatile Matter	Total Ash	Water-insoluble Ash	Acid-insoluble Ash	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	Nitro-gea	Crude Fiber	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
34	China	6.08	43.76	3.90	4.17	0.82	4.19	1.85	0.11	1.96	0.539	0.617	7.77	8.3	3.91	1.075		MgO	
35	China	6.25	37.52	4.39	4.31	0.71	3.89	3.03	0.48	1.28	0.448	0.449	7.81	7.7	2.28	0.797		MgO	
36	China	5.90	39.69	3.92	4.48	0.78	4.19	3.72	0.34	1.43	0.583	0.560	7.21	8.2	2.63	1.071		MgO	
37	China	7.26	33.70	4.28	4.26	...	8.41	7.99	4.86	1.62	0.488	0.498	7.25	7.2	2.74	0.826		MgO	
38	Japan	5.72	42.84	3.94	4.18	0.86	4.24	2.51	0.15	1.87	0.500	0.611	7.66	8.1	3.63	0.972		MgO	
39	Japan	6.15	40.10	4.07	4.25	0.81	4.33	3.83	0.76	1.39	0.513	0.485	7.57	7.9	2.59	0.954		MgO	
40	Japan	5.68	43.17	4.04	3.94	0.88	4.03	3.53	0.12	1.92	0.504	0.640	7.90	7.7	3.75	0.985		MgO	
41	Japan	6.33	39.15	4.02	4.20	0.67	4.23	3.09	0.20	1.86	0.457	0.559	7.41	7.7	3.43	0.843		MgO	
42	Orient	7.34	37.65	4.11	4.39	0.65	5.29	4.85	1.54	1.77	0.516	0.502	7.47	8.0	3.22	0.938		MgO	
43	Orient	7.02	38.17	4.04	4.28	0.78	5.60	5.01	1.85	1.63	0.529	0.500	7.37	7.8	2.97	0.965		MgO	
	Maximum	7.34	43.76	4.39	4.48	0.88	8.41	7.99	4.86	1.96	0.583	0.640	7.90	8.3	3.91	1.075		MgO	
	Minimum	5.68	33.70	3.90	3.94	0.65	3.89	1.85	0.11	1.28	0.448	0.449	7.21	7.2	2.28	0.797		MgO	

SAMPLE NO.	ORIGIN OF SEED	ON MOISTURE-, FAT-, AND ACID-INSOLUBLE ASH-FREE BASIS										RATIOS			
		Nitrogen	Crude Fiber	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	N	P <sub>2</sub> O <sub>5</sub> C. F.	MgO C. F.	CaO MgO	CaO×CF P <sub>2</sub> O <sub>5</sub> ×N	(A)	(B)		
		per cent	per cent	per cent	per cent	per cent	C. F.	C. F.	C. F.						
34	China	7.79	8.3	3.92	1.077	1.233	0.93	0.47	0.15	0.87	0.29	0.23			
35	China	7.87	7.7	2.30	0.804	0.805	1.02	0.30	0.10	1.00	0.34	0.42			
36	China	7.25	8.3	2.64	1.078	1.035	0.87	0.32	0.12	1.04	0.46	0.44			
37	China	7.90	7.9	2.99	0.901	0.919	1.00	0.38	0.12	0.98	0.30	0.33			
38	Japan	7.68	8.1	3.65	0.975	1.191	0.94	0.45	0.15	0.92	0.28	0.23			
39	Japan	7.68	8.0	2.62	0.968	0.915	0.96	0.33	0.11	1.06	0.38	0.41			
40	Japan	7.92	7.7	3.76	0.988	1.254	1.02	0.49	0.16	0.79	0.26	0.21			
41	Japan	7.44	7.8	3.44	0.846	1.035	0.96	0.44	0.13	0.82	0.26	0.25			
42	Orient	7.69	8.2	3.31	0.965	0.939	0.94	0.40	0.11	1.03	0.31	0.33			
43	Orient	7.63	8.1	3.08	0.999	0.944	0.94	0.38	0.12	1.06	0.34	0.36			
	Maximum	7.92	8.3	3.92	1.078	1.254	1.02	0.49	0.16	1.06	0.46	0.44			
	Minimum	7.25	7.7	2.30	0.804	0.805	0.87	0.30	0.10	0.79	0.26	0.21			

\*Chlorides in 2 samples—traces.  
Alkalinity, water-soluble ash, in 9 samples (cc. 0.1N acid per gram)—maximum, 1.30 cc.; minimum, 0.07 cc.  
Alkalinity, water-insoluble ash, in 9 samples (cc. 0.1N acid per gram)—maximum, 5.21 cc.; minimum, 1.87 cc.  
†On moisture-, fat-, and acid-insoluble ash-free basis.

TABLE  
Composition of mustard bran and flour, and comparison  
(Averages of dupli-

SAMPLE NO.	ORIGIN OF SEED	ON ORIGINAL MATERIAL										
		Moisture Vacuum 100°C.	Ether Extract	Nitrogen	Crude Fiber	Volatile Oil of Mustard	Total Ash	Water-insoluble Ash	Acid-insoluble Ash	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO
	<i>Brans</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
44	England..	10.15	10.24	2.39	19.24	....	4.98	2.93	0.14	0.60	1.339	0.297
45	England..	11.08	10.45	2.54	18.18	....	4.62	1.95	0.01	0.59	1.320	0.226
46	Japan....	10.17	13.88	3.12	14.14	0.33	5.01	3.54	0.26	0.95	1.235	0.352
	<i>Flour*</i>											
47	England..	5.74	38.47	4.92	1.63	0.06	4.41	3.00	0.17	2.44	0.473	0.570
<i>Values for whole</i>												
	Maximum	8.71	43.76	5.43	6.87	1.32	8.97	8.46	4.86	2.57	1.014	0.717
	Minimum	5.68	26.01	3.51	3.94	0.04	3.57	1.85	0.00	1.28	0.448	0.401

\*On moisture- and fat-free basis.

ash is high. The limits between which the values fluctuate are fairly close together. Ratios between certain of these values are also strikingly similar.

Table 3 gives the composition of three mustard brans and one mustard flour. Along with these, for comparative purposes, are given the maximum and minimum values for the composition of the mustard seed samples. The differences between the compositions of the brans and the seeds are considerable. Certain of the ratios also show large differences. In addition to the crude fiber, these ratios offer a means of detecting mustard bran in prepared mustard.

#### EXPERIMENTAL BATCHES OF PREPARED MUSTARD.

The data given are for use in interpreting the analyses of prepared mustards. Prepared mustard contains very finely ground mustard seed, spices, turmeric, vinegar, and salt. It seemed desirable to ascertain whether the data given on the seed can be directly applied to interpretation of analyses of prepared mustard, and whether the presence of the turmeric and spices, or the degree of fineness of grinding would seriously influence the percentage of crude fiber found by analysis in the finished article. Analysis of a prepared mustard of known composition and of the constituent seeds by the methods of this investigation should prove this point, it was thought. For this purpose two experimental

## 3.

with maximum and minimum values for whole seed.

(date determinations.)

ON MOISTURE- AND FAT-FREE BASIS					RATIOS					
Nitrogen	Crude Fiber	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	$\frac{N}{C. F.}$	$\frac{P_2O_5}{C. F.}$	$\frac{MgO}{C. F.}$	$\frac{CaO}{MgO}$	(A) $\frac{CaO \times CF}{P_2O_5 \times N}$	(B) $\frac{A}{MgO^*}$
per cent	per cent	per cent	per cent	per cent						
3.00	24.2	0.75	1.682	0.373	0.12	0.03	0.01	4.51	18.0	48.2
3.24	23.2	0.75	1.682	0.288	0.14	0.03	0.01	5.84	16.0	55.5
4.11	18.6	1.25	1.626	0.463	0.22	0.07	0.02	3.51	5.9	12.7
8.82	2.9	4.37	0.848	1.022	3.02	1.50	0.35	0.83	0.06	0.06

seed (all varieties).

8.35	11.0	4.40	1.734	1.326	1.00	0.49	0.16	1.71	0.78	0.88†
6.42	7.2	2.28	0.734	0.616	0.56	0.28	0.07	0.79	0.26	0.21

†On fat- and salt-free solids basis, or fat-, salt-, and acid-insoluble ash-free solids basis.

lots of prepared mustards were made up at two factories under supervision of the writer, and samples of the seeds and final product were taken for analysis.

Prepared mustard, Sample 50, was made according to the following formula:

150 pounds of California yellow seed (Sample 16);

150 pounds of California brown seed (Sample 30);

3 pounds of black pepper;

3 pounds of cloves;

3 pounds of allspice;

2 pounds of coriander;

24 pounds of salt;

8 pounds of turmeric; and

170 gallons of distilled vinegar.

The seeds and spices, after being coarsely ground by a power mill and transferred to a mixing tank containing the salt and vinegar, were mixed by a motor-driven paddle. This mixture was then pumped immediately to two sets of stones for the final grinding. Portions taken at intervals just before the mixture entered the stones were combined for analysis, Sample 50. Portions of the final product, issuing from the second set of stones and taken at regular intervals, were combined for Sample 48.

TABLE  
Composition of prepared mustards made  
(Averages of dupli-

SAMPLE NO.	DESCRIPTION OF SAMPLE (Relative amounts of seeds used in the formulas are indicated.)	ON ORIGINAL MATERIAL										
		Moisture Vacuum 100°C	Ether extract	Nitro- gen	Crude Fiber	Total Ash	Water- insolu- ble Ash	Acid- insolu- ble Ash	Salt	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO

(First

30	California brown seed (1 part) ..	8.19	31.38	4.71	4.81	4.38	3.91	0.08	....	1.81	0.553	0.568
16	California yellow seed (1 part) ..	8.22	29.50	4.56	5.57	5.47	4.66	0.12	....	2.57	0.755	0.542
	(Theoretical values for mixture of 1 part Sample 30 and 1 part Sample 16).	....	....	....	....	....	....	....	....	....	....	....
48	Prepared mustard (final product)	81.84	5.24	0.768	1.03	2.35	0.68	0.02	1.36	0.368	0.129	0.111

(Second

13	California yellow seed (2 parts)	8.71	26.01	5.18	5.34	3.68	3.12	0.09	....	1.56	0.535	0.445
27	California brown seed (1 part) ..	7.85	37.76	3.84	5.44	4.64	3.99	0.25	....	2.27	0.605	0.717
37	Oriental seed (2 parts) .....	7.26	33.70	4.28	4.26	8.41	7.99	4.86	....	1.62	0.488	0.498
	(Theoretical values for mixture of 2 parts Sample 13, 1 part Sample 27, and 2 parts Sample 37).	....	....	....	....	....	....	....	....	....	....	....
49	Prepared mustard .....	78.79	5.31	0.776	1.03	4.74	0.98	0.38	3.44	0.307	0.114	0.096

\*As per cents of fat-, salt-, and acid-insoluble ash-free solids.

†On fat- and salt-free solids basis.

A second sample of prepared mustard (Sample 49) was made according to the following formula:

100 pounds of Chinese yellow seed (Sample 37);  
 100 pounds of California yellow seed (Sample 13);  
 50 pounds of California brown seed (Sample 27);  
 5 pounds of spice;  
 1.5 pounds of cayenne pepper;  
 30 pounds of turmeric; and  
 70 pounds of salt.

The method of manufacture was essentially that of Sample 48. The mixture was passed twice through a set of stones for grinding. Portions of the final product issuing from the stones, taken at regular intervals, were combined for this sample.

The prepared mustards were analyzed according to the methods in Chapter XXIII, *Prepared Mustards*, except that the total solids were determined in vacuo at 100°C., and the crude fiber was determined by the Hilts-Hertwig modification of the general crude fiber method, previously described.

The compositions of the prepared mustards and their respective seeds are given in Table 4.

4.

*under supervision and of seed used.**cate determinations.)*

FAT-SALT-FREE SOLIDS BASIS					RATIOS					
Nitrogen	Crude Fiber	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	$\frac{N}{C. F.}$	$\frac{P_2O_5}{C. F.}$	$\frac{MgO}{C. F.}$	$\frac{CaO}{MgO}$	$\frac{(A)}{CaO \times C.F.}$ $\frac{P_2O_5 \times N}{P_2O_5 \times N}$	$\frac{(B)}{A}$ $\frac{A}{MgO \dagger}$
Experiment)										
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>						
7.79	8.0	3.00	0.915	0.940	0.98	0.38	0.12	0.97	0.31	0.33
7.32	8.9	4.13	1.212	0.934	0.82	0.46	0.10	1.39	0.36	0.38
(7.55)	(8.45)	(3.56)	(1.063)	(0.937)	(0.90)	(0.42)	(0.11)	(1.18)	(0.33)	(0.35)
6.64	8.9	3.18	1.116	0.960	0.75	0.36	0.11	1.16	0.47	0.49
Experiment)										
7.93	8.2	2.39	0.820	0.682	0.97	0.29	0.08	1.20	0.35	0.51
7.06	10.0	4.17	1.112	1.318	0.71	0.42	0.13	0.84	0.38	0.29
7.90*	7.9*	2.99*	0.901*	0.919*	1.00	0.38	0.12	0.98	0.30	0.33†
(7.74)	(8.4)	(2.99)	(0.911)	(0.904)	(0.93)	(0.35)	(0.11)	(1.04)	(0.34)	(0.39)
6.42*	8.5*	2.54*	0.944*	0.795*	0.75	0.30	0.09	1.19	0.49	0.62†

†On fat-, salt-, and acid-insoluble ash-free solids basis.

## DISCUSSION OF TABLE 4.

Comparison of the compositions of the prepared mustards, on the fat-, salt- (acid-insoluble ash-, Sample 49) free solids basis, with the theoretical values for mixtures of their respective seeds, in proportions as used in the prepared mustards on the same basis, shows the following:

The nitrogen of the prepared mustards is quite markedly lower, the crude fiber slightly higher, the phosphoric acid slightly lower, the calcium oxide slightly higher, and the magnesium oxide slightly higher in one instance and lower in the other, than the theoretical values for the seeds used. In general, the agreement is good and all that can be expected. The slight differences noted are doubtless explained by the spices present in the mixtures. It may be concluded from this that the crude fiber results from the seeds, given in Tables 1 and 2, may be used in interpreting the analyses of prepared mustards. Another very significant conclusion which may be drawn from these two experiments is that the method proposed for determining crude fiber in prepared mustard, with previous extraction of fat, gives reliable results which are concordant with the crude fiber content of the mustard seed used.

In Table 5 are brought together all the ratios and significant values in the preceding tables to facilitate the interpretation of analyses. For

TABLE 5.  
*Summary of preceding tables.*

DESCRIPTION OF SAMPLE	FAT*, SALT*, ACID-INSOLUBLE ASH-FREE SOLIDS BASIS						RATIOS				
	Nitro- gen	Crude Fiber	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	N	P <sub>2</sub> O <sub>5</sub> C. F.	MgO C. F.	CaO MgO	(A) $\frac{\text{CaO} \times \text{C.F.}}{\text{P}_2\text{O}_5 \times \text{N}}$	(B) $\frac{\text{A}}{\text{MgO}^*}$
	per cent	per cent	per cent	per cent	per cent						
Seeds.....Maximum	8.35	11.0	4.40	1.734	1.326	1.00	0.49	0.16	1.71	0.78	0.88
Seeds.....Minimum	6.42	7.2	2.28	0.734	0.616	0.56	0.28	0.07	0.79	0.26	0.21
Brans.....English	3.00	24.2	0.75	1.682	0.373	0.12	0.03	0.01	4.51	18.0	48.2
Brans.....English	3.24	23.2	0.75	1.682	0.288	0.14	0.03	0.01	5.84	16.0	55.5
Brans.....Japanese	4.11	18.6	1.25	1.626	0.463	0.22	0.07	0.02	3.51	5.9	12.7
<i>First Experiment.</i>											
Prepared mustard (known composition) .....	6.64	8.9	3.18	1.116	0.960	0.75	0.36	0.11	1.16	0.47	0.49
Theoretical values for mixture of seeds used...	7.55	8.4	3.56	1.063	0.937	0.90	0.42	0.11	1.18	0.33	0.35
<i>Second Experiment.</i>											
Prepared mustard (known composition) .....	6.42	8.5	2.54	0.944	0.795	0.75	0.30	0.09	1.19	0.49	0.62
Theoretical values for mixture of seeds used...	7.74	8.4	2.99	0.911	0.904	0.93	0.35	0.11	1.04	0.34	0.39

\*On fat- and salt-free solids basis, or fat-, salt-, and acid-insoluble ash-free solids basis.

interpretation of analyses of prepared mustard the following procedure is suggested:

The analyses should first be calculated to the fat- and salt-free solids basis. If the product contains 0.10 per cent or more of acid-insoluble ash it should be calculated to the fat-, salt-, and acid-insoluble ash-free solids basis. Also calculate the various ratios suggested. The analyses on this common basis and also the ratios are then compared with the analyses and ratios of the commercial mustard seeds as summarized in Table 5. The highest crude fiber found in the seeds on the moisture- and fat-free solids basis was 11 per cent. However, since the crude fiber determination is influenced by various factors, and because it appears that the crude fiber in the prepared mustard may be slightly higher on account of the spices used, it is quite possible that an unadulterated prepared mustard may contain slightly over 11 per cent of crude fiber. It must be remembered, however, that prepared mustards containing less than 11 per cent crude fiber may still be considerably adulterated with bran. A comparison of the various ratios of the sample in question with the same ratios for seeds and for brans will give additional indication of the presence of bran and may help to confirm its presence where the crude fiber figure alone is not conclusive. It is believed that all the suggested ratios will give a positive indication when a considerable proportion of bran is present. In the interpretation of analyses the possible differences between the analysis and ratios of a given prepared mustard and of the seeds entering into it, as illustrated by the two experimental lots of prepared mustard shown in the table, must be kept in mind.

Table 6 presents the analyses of 15 commercial prepared mustards.

#### DISCUSSION OF TABLE 6.

The first five samples (51-55) are clearly adulterated with considerable quantities of added mustard bran. The crude fiber and all six of the ratios clearly show this.

In Sample 56 the nitrogen and crude fiber values on the fat- and salt-free solids basis are within the limits for the present standard for prepared mustard<sup>1</sup>. Four out of the six ratios, however, indicate definitely adulteration with at least small amounts of mustard bran. It was ascertained that Japanese bran had been used in this product.

In Sample 57, on the moisture-, fat-, and salt-free solids basis, the nitrogen figure agrees with that of the present standard, and the crude fiber value is 0.7 higher than that of the standard. Judged according to the standard alone, the product would fall under suspicion as containing small amounts of added bran. However, five out of the six

<sup>1</sup> U. S. Dept. Agr. Circ. 136, Office of the Secretary.



TABLE  
*Composition of commercial prepared*

SAMPLE NO.	ON ORIGINAL MATERIAL								
	Solids 100°C.	Ether Extract	Nitrogen	Crude Fiber	Water-Insoluble Ash	Salt	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
51	15.95	4.29	0.497	1.30	0.59	2.36	0.199	0.148	0.069
52	13.78	3.26	0.387	1.09	0.40	2.89	0.181	0.121	0.055
53	13.14	3.15	0.362	1.12	0.41	2.72	0.138	0.139	0.050
54	16.32	4.50	0.513	1.32	0.55	2.39	0.194	0.138	0.071
55	13.36	3.25	0.382	1.24	0.38	2.77	0.152	0.126	0.053
56	16.77	4.74	0.649	1.27	0.56	1.27	0.248	0.129	0.087
57	16.40	4.58	0.626	1.34	0.57	1.31	0.233	0.167	0.097
58	17.89	4.95	0.796	1.07	0.59	1.28	0.275	0.156	0.093
59	23.50	8.68	0.961	0.94	0.92	0.76	0.450	0.136	0.152
					(Acid-Insoluble Ash)				
60	19.13	5.71	0.920	0.95	0.048	1.20	0.292	0.108	0.087
61	22.70	4.68	0.809	1.00	0.037	5.24	0.338	0.145	0.110
62	15.14	3.49	0.628	0.81	0.031	2.27	0.288	0.112	0.080
63	22.63	6.43	0.905	1.12	0.02	1.64	0.392	0.158	0.103
64	23.10	6.30	0.895	1.01	0.02	4.10	0.415	0.156	0.121
65	17.92	4.44	0.698	1.06	0.01	2.36	0.321	0.107	0.102

\*On fat-and salt-free solids basis.

ratios indicate that the product is adulterated with bran. It was also ascertained that Japanese bran had been used in this product.

The analyses and ratios of the remaining samples are not indicative of adulteration with added mustard bran.

#### SUMMARY AND CONCLUSION.

(1) Analyses are given of 43 commercial mustard seeds. For comparison there are included 3 mustard brans, 1 mustard flour, 2 prepared mustards of known composition, and 15 commercial prepared mustards.

(2) Coarsely ground seed yields slightly lower ether extract than finely ground seed.

(3) Degree of fineness of division of mustard seed affects the crude fiber determination. Defatted seed ground in a mortar with a pestle shows a crude fiber content similar to that of the same seed made into a prepared mustard by the usual commercial process.

(4) The analyses of two prepared mustards of known composition did not differ notably from the analyses of their respective seeds. The addition of spices to seeds, in amounts as used in prepared mustards, modifies only slightly the composition of the final product.

## 6.

*mustards of unknown constitution.*

ON FAT-SALT-FREE SOLIDS BASIS					RATIOS					
Nitrogen	Crude Fiber	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	$\frac{N}{C. F.}$	$\frac{P_2O_5}{C. F.}$	$\frac{MgO}{C. F.}$	$\frac{CaO}{MgO}$	$\frac{(A) CaO \times CF}{P_2O_5 \times N}$	$\frac{(B) A}{MgO^*}$
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>						
5.34	14.0	2.14	1.591	0.742	0.38	0.15	0.05	2.14	1.94	2.61
5.07	14.3	2.37	1.586	0.721	0.35	0.17	0.05	2.20	1.88	2.61
4.98	15.4	1.90	1.912	0.688	0.32	0.12	0.04	2.78	3.12	4.53
5.44	14.0	2.06	1.463	0.753	0.39	0.15	0.05	1.94	1.83	2.43
5.20	16.9	2.07	1.717	0.722	0.31	0.12	0.04	2.38	2.69	3.73
6.03	11.8	2.30	1.199	0.809	0.51	0.19	0.07	1.48	1.02	1.26
5.96	12.7	2.22	1.589	0.923	0.47	0.17	0.07	1.72	1.53	1.66
6.83	9.2	2.36	1.338	0.798	0.74	0.26	0.09	1.68	0.76	0.95
6.83	6.7	3.20	0.967	1.081	1.02	0.48	0.16	0.89	0.29	0.27
7.53	7.8	2.39	0.884	0.712	0.97	0.31	0.09	1.24	0.38	0.53
6.33	7.8	2.64	1.135	0.861	0.81	0.34	0.11	1.32	0.53	0.62
6.69	8.6	3.07	1.194	0.853	0.77	0.36	0.10	1.40	0.50	0.59
6.21	7.7	2.69	1.085	0.707	0.81	0.35	0.09	1.53	0.50	0.71
7.05	7.9	3.27	1.228	0.953	0.89	0.41	0.12	1.29	0.43	0.45
6.28	9.5	2.89	0.962	0.917	0.66	0.30	0.10	1.05	0.50	0.54

(5) The mustard seeds analyzed are all quite uniform in their composition. Ratios between certain constituents are also quite uniform. The composition of mustard brans and the ratios between certain constituents differ greatly from those of mustard seed. These differences offer a means of detecting added bran in prepared mustards.

(6) The nitrogen and crude fiber content of a prepared mustard alone is insufficient to detect adulteration with mustard bran in some cases. Certain ratios between the nitrogen, crude fiber, total phosphoric acid, calcium oxide, and magnesium oxide, will often indicate the presence of added bran even when the crude fiber is not excessive.

(7) With prepared mustards suspected of containing added bran, determinations should be made for solids, nitrogen, crude fiber (Hilts-Hertwig), ether extract, acid-insoluble ash, chlorides as sodium chloride, total phosphoric acid (by method described), calcium oxide, and magnesium oxide. A microscopical examination should also be made.

## THE DIFFERENTIATION OF NOODLES MADE WITH WHOLE EGG FROM THOSE MADE WITH YOLK.

By RAYMOND HERTWIG<sup>1</sup> (Food and Drug Inspection Station, San Francisco, Calif.).

Noodles, or egg noodles, are defined by Circular 136, U. S. Department of Agriculture, Office of the Secretary, as "dried alimentary pastes containing not less than five per cent by weight of the solids of whole sound egg exclusive of shell". During recent years the inspection of noodle factories has disclosed the frequent substitution of commercial egg yolk for whole egg, contrary to the commonly accepted definition. The use of yolk in noodles gives the manufacturer two advantages: First, yolk is cheaper than whole egg; second, as the lecithin of egg is present in the yolk only, considerably less yolk than whole egg is necessary to make a noodle corresponding to the standard noodle in lecithin content. It is upon this lecithin content that the food analyst places principal reliance for estimating the proportion of egg solids present.

The chemical differences between yolk and whole egg cause corresponding differences in the composition of noodles made from them. Whole egg solids contain considerably more total protein and albumin, and less lecithin and fat than do yolk solids<sup>2</sup>. Total nitrogen, albumin nitrogen, fat, and lecithin were decided upon as the determinations essential for distinguishing between yolk and whole egg noodles.

Search of chemical literature did not reveal any methods which seemed directly applicable to the determination of albumin nitrogen and fat in the products under consideration. Rousseaux and Sirot<sup>3</sup> used hot water extractions of flours for estimating water-soluble nitrogen and found a definite relation between water-soluble nitrogen and total nitrogen in good flours. Nockmann<sup>4</sup> noted that the recovery of the ether extract of a noodle is less than that calculated from its constituent materials. Schmid<sup>5</sup> suggested the determination of the soluble albumin of noodles as a means of determining the egg solids content and also whether yolk or whole egg had been used. He extracted 30 grams by shaking 30 minutes with 150 cc. of water. Twenty cc. of extract were heated at 85°C. for 10 minutes, 2 cc. of 10 per cent nitric acid were added, and the mixture was centrifuged. The volume of the precipitate compared to a control determination was used to estimate the egg solids content of the sample.

<sup>1</sup> The writer wishes to acknowledge the criticisms and suggestions of R. W. Hiltz, Chief, Food and Drug Inspection, Western District, in connection with this investigation.

<sup>2</sup> Leach. Food Inspection and Analysis, 1920, 269; Juckmack, *Z. Nahr. Genussm.*, 1899, 2: 905.

<sup>3</sup> *Ann. fals.*, 1913, 6: 78; 1917, 10: 556.

<sup>4</sup> *Z. Nahr. Genussm.*, 1913, 25: 717.

<sup>5</sup> *Chem. Z.*, 1912, 36: 796.

The methods finally devised by the writer for these determinations are as follows:

#### METHODS APPLICABLE TO FLOURS AND NOODLES.

##### *Water-soluble nitrogen.*

Place 20 grams of finely ground sample in an 8 oz. nursing bottle, add about 100 cc. of distilled water from a 200 cc. pipet, shake the bottle violently a few times to prevent lumping of the sample, and add the remainder of the 200 cc. Shake the stoppered bottle in a machine for one-half hour. The temperature should be between 20° and 30°C. Centrifuge the bottle to facilitate filtration and filter through a thin asbestos pad in a Hirsch funnel, using light suction. Replace the asbestos if it clogs. The filtrate should be practically clear. Determine the nitrogen in 50 cc. of the filtrate by the Gunning<sup>1</sup> method. Use 20 cc. of 0.1N acid to receive the ammonia in the distillate. Make blank determinations on the reagents.

Water-soluble nitrogen determined by this method represents principally the albumin, proteose, amino acids, and a portion of the globulin<sup>2</sup>.

If the extraction is made at 45° to 50°C., results are slightly higher than 20° to 30°C. Three-hour, one-hour, and one-half-hour periods of shaking, variations of sample from 12 to 25 grams, preliminary extraction of the fat before extraction with water, and the absence or presence of salt up to the equivalent of 1.6 per cent on the sample weight do not materially affect the results.

##### *Water-soluble nitrogen precipitated by alcohol.*

Pipet 50 cc. of the water extract obtained as shown in the preceding method into a 125 cc. beaker flask or Erlenmeyer flask. Add 0.6 gram of sodium chloride and dissolve. Add a small amount of finely divided filter paper pulp or asbestos, shake, and, with constant agitation, add 35 cc. of 95 per cent alcohol. Allow to stand overnight. Filter the mixture through a mat of paper pulp or asbestos on a Hirsch funnel, using light suction. Wash the precipitate three times with 40 per cent alcohol. Transfer the filter mat with the precipitate to a Kjeldahl flask and determine the nitrogen by the Gunning method. Use 10 cc. of 0.1N acid to receive the ammonia in the distillate. Make a blank determination on the reagents and the filter paper pulp or asbestos.

Prepare the paper pulp by shredding filter paper, macerating in hot water, and shaking in a bottle with glass beads until well disintegrated. Remove the water by filtering and suspend in 40 per cent alcohol for use. Prepare asbestos by igniting and rubbing through on an 8-mesh sieve.

The proportions of water and alcohol used in the method give a mixture of about 40 per cent alcoholic strength. According to Mann<sup>3</sup> and Tebb<sup>4</sup> this concentration of alcohol, in the presence of a small amount of sodium chloride, gives complete precipitation of albumin, but does not precipitate proteoses and many other proteins. This determination is accordingly an index of the proportion of water-soluble albumin present.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 7.

<sup>2</sup> Osborne, T. B. *Proteins of the Wheat Kernel*—Carnegie Institution of Washington, Publication No. 84.

<sup>3</sup> *Methods and Theory of Physiological Histology*, 1902, 103.

<sup>4</sup> *J. Physiol.*, 1903, 36: 25.

It was found also by experiment that 40 per cent strength of alcohol gave the best differentiation between flours, yolk noodles, and whole egg noodles. The salt aids in the flocculation of the precipitate.

*Fat by acid digestion method.*

Place 2 grams of ground sample in a 50 cc. beaker, add 2 cc. of 95 per cent alcohol and stir so as to moisten all particles. Add 10 cc. of hydrochloric acid (sp. gr., 1.125), mix well, immerse the beaker in a water bath held at about 65°C. and stir at frequent intervals for 15 to 25 minutes, or until the proteins and starch are sufficiently hydrolyzed to form a clear solution. Add 10 cc. of 95 per cent alcohol and cool. Transfer the mixture to a Röhrig tube or a Mojonnier fat extraction tube; rinse out the beaker with 25 cc. of washed ethyl ether, in three portions, and shake well. Add 25 cc. of redistilled petroleum ether (b. p. below 60°C.) and mix well. From here proceed as directed under the official Roese-Gottlieb method for fat in milk<sup>1</sup>, re-extracting twice more with 15 cc. of each ether.

The moistening of the sample with alcohol prevents lumping on addition of the acid. This method, devised by the writer, has been found to give higher results on flours, alimentary pastes, eggs and noodles, than the method of direct extraction with ether, and to give practically complete recovery of the fat of noodles as calculated from their constituent materials. It is not suitable, however, for the extraction of lecithin-phosphoric acid.

*Lecithin-phosphoric acid.*

Lecithin-phosphoric acid was determined in this investigation by the method of Juckenack<sup>2</sup>, which does not give complete extraction of the lecithin or lipins of flours, noodles and possibly eggs. At the time this investigation was made no other method was available. Since then methods for estimating lipin-phosphoric acid, giving much higher results, have been proposed by Rask and Phelps, in an unpublished paper, and by the writer, page 92. Future work of this nature should employ one of these improved methods.

Determine total nitrogen in a two-gram sample by the Gunning method.

METHODS APPLICABLE TO DRIED EGGS.

*Water-soluble nitrogen.*

Defat 5 grams of sample on a filter with ether. Allow the ether to evaporate spontaneously. Transfer the sample to a nursing bottle and proceed with the method as described in the preceding paragraphs. Use 30 cc. of 0.1N acid to receive the ammonia distillate.

Unless the fat is first removed the water extract can not be filtered clear, and concordant results can not be obtained.

<sup>1</sup> Assoc. Official Agr. Chemists, Methods, 1920, 227.

<sup>2</sup> Leach. Food Inspection and Analysis, 1920, 366; Z. Nahr. Genussm., 1900, 3: 1.

Determine the alcohol-precipitable nitrogen as previously described. Use 30 cc. of 0.1N acid to receive the ammonia distillate.

Determine the lecithin-phosphoric acid in a 5-gram sample. Determine the fat and the total nitrogen by the method for flours, previously described.

### COMPOSITION OF FLOURS.

Table 1 gives the analyses, by the methods presented, of 20 flours and semolinas. These are divided roughly into three groups. Ratios given between certain constituents, expressed as percentages, are those which have been found of most assistance in interpreting the analyses of noodles.

TABLE 1.  
*Composition of flours and semolinas.*

SAMPLE NO.	Total Nitrogen	Water-soluble Nitrogen	Alcohol-Precipitable Nitrogen	Fat (Acid Method)	Lecithin $P_2O_5$ (Juckmack Method)	$\frac{\text{Water-soluble nitrogen}}{\text{Total nitrogen}}$	$\frac{\text{Alcohol-precipitable nitrogen}}{\text{Total nitrogen}}$	$\frac{\text{Lecithin } P_2O_5}{\text{Alcohol-precipitable nitrogen}}$	$\frac{\text{Alcohol-precipitable nitrogen}}{\text{Fat (acid method)}}$
(1) <i>Semolinas from noodle and macaroni factories.</i>									
1	2.10	0.257	0.054	1.86	0.0235	12.2	2.6	43.5	2.9
2	2.10	0.235	0.049	1.93	0.0319	11.2	2.3	65.1	2.5
3	2.16	0.245	0.049	1.86	0.0292	11.3	2.3	59.6	2.6
4	2.24	0.247	0.039	1.83	0.0262	11.0	1.7	67.2	2.1
5	2.06	0.268	0.055	....	....	13.0	2.7	....	...
6	2.28	0.281	....	1.77	0.0291	12.3	...	....	...
(2) <i>Flours from noodle and macaroni factories.</i>									
7	2.03	0.293	0.032	1.75	0.0293	14.4	1.6	91.6	1.8
8	2.03	0.281	0.052	2.09	0.0274	13.8	2.6	52.7	2.5
9	2.84	0.385	0.077	2.50	0.0327	13.5	2.7	42.5	3.1
10	1.86	0.268	0.024	1.56	0.0264	14.4	1.2	110.0	1.5
11	2.14	0.258	0.047	2.13	0.0317	12.0	2.2	67.5	2.2
12	2.29	0.304	0.055	2.02	0.0333	13.3	2.4	60.5	2.7
13	2.34	0.302	0.028	....	....	12.9	1.2	....	...
14	2.08	0.286	0.054	....	....	13.8	2.6	....	...
(3) <i>Patent flours.</i>									
15	1.89	0.283	0.024	....	....	15.0	1.3	....	...
16	2.02	0.229	0.026	....	....	11.4	1.3	....	...
17	1.95	0.246	0.032	....	....	12.6	1.6	....	...
18	1.94	0.304	0.016	....	....	15.7	0.8	....	...
19	1.92	0.250	0.028	....	....	13.1	1.5	....	...
20	1.88	0.263	0.023	....	....	14.0	1.2	....	...

## COMPOSITION OF EGGS, LIQUID AND DRIED.

The analyses of three commercial egg yolk and three whole egg samples are given in Table 2. The water-soluble nitrogen of the fresh liquid eggs (Sample 21) on the dry basis is 3.93 per cent. The two dried whole egg samples (22 and 23) have, on the dry basis, 3.98 and 3.71 per cent water-soluble nitrogen. Apparently the drying of the eggs has not affected the solubility of the albumin. The differences in the composition between the yolk and whole egg are to be noted. The ratios make these differences very striking.

TABLE 2.  
*Composition of eggs.*

SAMPLE NO.	SAMPLE	SOLIDS (VACUUM 55°C.)	TOTAL NITROGEN	WATER-SOLUBLE NITROGEN	ALCOHOL-PRECIPTABLE NITROGEN	FAT (ACID METHOD)	LECITHIN $P_2O_5$ (JUCKENACK METHOD)	Water-soluble nitrogen Total nitrogen	Alcohol-precipitable nitrogen Total nitrogen	Lecithin $P_2O_5$ Alcohol-precipitable nitrogen	Alcohol-precipitable nitrogen Fat (acid method)
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
21	Fresh whole egg . . . .	28.80	2.21	1.133	....	....	0.3777	51.2	...	....	...
22	Dried whole egg . . . .	94.33	7.18	3.754	....	42.39	1.341	52.3	...	....	...
23	Dried whole egg . . . .	93.03	6.94	3.453	2.573	41.53	1.2697	49.7	37.1	49.3	6.2
24	Dried commercial yolk	94.70	5.30	1.636	0.705	53.38	1.6876	30.9	13.3	239.4	1.3
25	Fresh commercial yolk	39.28	2.36	0.786	....	....	0.6677	33.3	...	....	...
26	Dried commercial yolk	94.77	4.91	1.008	0.465	57.23	1.7548	20.5	9.5	377.4	0.8

COMPARISON OF COMPOSITIONS OF THE EGGS AND FLOURS  
ANALYZED.

Table 3 gives the maximum and minimum ratios of the flours of Table 1 and similar ratios for whole eggs and yolks of Table 2. The differences between the ratios for flour, whole egg, and yolk are self-evident.

TABLE 3.  
*Results showing comparison of ratios of flours and eggs.*

	FLOUR <i>per cent</i>	WHOLE EGGS <i>per cent</i>	YOLKS <i>per cent</i>
Water-soluble nitrogen			
Total nitrogen	11.0-15.7	49.7-52.3	20.5-33.3
Alcohol-precipitable nitrogen			
Total nitrogen	0.8-2.7	37.1	9.5-13.3
Lecithin $P_2O_5$ (Juckcnack)			
Alcohol-precipitable nitrogen	42.5-110.0	49.3	239.4-377.4
Alcohol-precipitable nitrogen			
Fat (Acid method)	1.5-3.1	6.2	0.8-1.3

TABLE 4.  
*Composition of noodles and of the flours from which they were made.*

SAMPLE NO.	DESCRIPTION	EGG SOLIDS CONTENT (dry basis)	TOTAL NITROGEN	WATER-SOLUBLE NITROGEN	ALCOHOL-PRECIPTABLE NITROGEN	FAT (Acid Method)	LECITHIN P <sub>2</sub> O <sub>5</sub> (Juckensch Method)	Water-soluble nitrogen Total nitrogen	Alcohol-precipitable nitrogen Total nitrogen	Alcohol-precipitable nitrogen Lecithin P <sub>2</sub> O <sub>5</sub> (Juckensch)	Alcohol-precipitable nitrogen Fat (acid method)
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
27	Whole Egg Noodles (Fresh Eggs) . . . . .	8.76	2.34	0.539	0.276	4.84	0.1002	23.1	11.8	36.3	5.7
7	Flour used . . . . .	..	2.03	0.293	0.032	1.75	0.0293	14.4	1.6	91.6	1.8
28	Whole Egg Noodles (Fresh Eggs) . . . . .	4.33	2.13	0.397	0.141	3.22	0.0480	18.7	6.6	34.0	4.4
7	Flour used . . . . .	..	2.03	0.293	0.032	1.75	0.0293	14.4	1.6	91.6	1.8
29	Whole Egg Noodles (Dried egg) . . . . .	4.98	2.42	0.398	0.192	3.77	0.0613	16.4	7.9	31.9	5.1
3	Semolina used . . . . .	..	2.16	0.245	0.049	1.86	0.0293	11.3	2.3	59.6	2.6
30	Whole Egg Noodles (Liquid Egg) . . . . .	2.86*	2.40	0.384	0.123	2.59	0.0352	16.0	5.1	28.6	4.7
4	Semolina used . . . . .	..	2.24	0.247	0.039	1.83	0.0262	11.0	1.7	67.2	2.1
31	Yolk Noodles (Dried yolk) . . . . .	5.35	2.25	0.332	0.064	4.33	0.0942	14.7	2.8	147.2	1.5
1	Semolina used . . . . .	..	2.10	0.257	0.051	1.86	0.0235	12.2	2.6	43.5	2.9
32	Yolk Noodles (Dried yolk) . . . . .	5.07	2.31	0.398	0.065	4.24	0.0739	13.8	2.8	113.7	1.5
2	Semolina used . . . . .	..	2.11	0.235	0.049	1.93	0.0319	11.2	2.3	65.1	2.5

\*An average percentage of solids in whole egg was used in the calculation as the sample of liquid whole egg was not available.



## ANALYSES OF NOODLES OF KNOWN COMPOSITION.

Table 4 gives the analyses of four whole egg noodles and two yolk noodles, of known composition, made at noodle factories under the direction of the writer or other members of the Bureau of Chemistry. Analyses of the flours used are given in conjunction with each noodle analysis, and also the calculated egg solids content, from the factory formulas.

The recovery of lecithin-phosphoric acid from the noodles, where complete data on composition of the component ingredients were known, ranged from 65 to 88 per cent of the theoretical, as calculated from the factory formulas. More accurate methods devised by the writer, page 92, and by Phelps and Rask, unpublished, for determining the lecithin-phosphoric acid will alter the ratio involving this constituent.

The differences between the ratios of the noodles and of their component flours, divided by the respective egg solids content on the dry basis, are given in Table 5, which shows how each added per cent of yolk or whole egg solids alters the ratios of the respective flours used.

TABLE 5.  
*Ratio differences.*

SAMPLE NO.	DESCRIPTION	$\frac{\text{Water-soluble nitrogen}}{\text{Total nitrogen}}$	$\frac{\text{Alcohol-precipitable nitrogen}}{\text{Total nitrogen}}$	$\frac{\text{Lecithin P}_2\text{O}_5 \text{ (Juckenaek)}}{\text{Alcohol-precipitable nitrogen}}$	$\frac{\text{Alcohol-precipitable nitrogen}}{\text{Fat (acid method)}}$
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
27	Whole Egg Noodle...	+0.99	+1.16	-6.31	+0.45
28	Whole Egg Noodle...	+0.99	+1.15	-13.30	+0.60
29	Whole Egg Noodle...	+1.02	+1.12	-5.56	+0.50
30	Whole Egg Noodle...	+1.75	+1.19	-13.50	+0.91
31	Yolk Noodle.....	+0.47	+0.04	+23.93	-0.32
32	Yolk Noodle.....	+0.51	+0.10	+9.59	-0.20

## SUMMARY.

Methods proposed for differentiating yolk noodles from whole egg noodles are given as follows:

Total nitrogen;  
Water-soluble nitrogen;  
Alcohol-precipitable nitrogen;  
Fat by acid digestion method; and  
Lecithin-phosphoric acid.

The determination of water-soluble nitrogen is of least assistance and may be omitted in routine analyses. The lecithin-phosphoric acid should be determined either by the more recent method proposed by the writer, page 92, or by that of Phelps and Rask, as yet unpublished.

Samples of flour, egg yolk, whole egg, yolk noodles and whole egg noodles were analyzed by the above methods. The compositions of all these materials differ markedly. These differences are well shown by ratios between certain ingredients. These ratios are:

- (1)  $\frac{\text{Water-soluble nitrogen} \times 100}{\text{Total nitrogen}}$ ;
- (2)  $\frac{\text{Alcohol-precipitable nitrogen} \times 100}{\text{Total nitrogen}}$ ;
- (3)  $\frac{\text{Lecithin-phosphoric acid} \times 100}{\text{Alcohol-precipitable nitrogen}}$ ; and
- (4)  $\frac{\text{Alcohol-precipitable nitrogen} \times 100}{\text{Fat, acid digestion method}}$ .

Ratio (1) is least important and may be omitted in routine analyses. The ratios are capable of differentiating yolk noodles from whole egg noodles when the noodles contain material amounts of the egg solids.

## DETERMINATION OF LIPOIDS AND LIPOID-PHOSPHORIC ACID IN FLOURS, ALIMENTARY PASTES, NOODLES AND EGGS.

By RAYMOND HERTWIG<sup>1</sup> (Food and Drug Inspection Station,  
San Francisco, Calif.).

Fat and lecithin-phosphoric acid determinations are essential in noodle analyses. Fat has been determined by extraction of the dry ground sample with absolute ether<sup>2</sup>. Lecithin-phosphoric acid has been determined by hot absolute alcohol extraction, according to Juckenack<sup>3</sup> and Beytheim and Wrampelmeyer<sup>4</sup> and phosphoric acid determined in the extract.

Dry ether extraction of alimentary pastes and noodles recovers only partially the fat of the component materials, as determined by Nockmann<sup>5</sup> and the writer<sup>6</sup>. Fat determined by an acid digestion method of the writer<sup>6</sup> extracts more fat from flours, alimentary pastes, noodles and

<sup>1</sup> Acknowledgment is made of the writer's appreciation of the criticism of this manuscript by R. W. Hiltz, Chief, Food and Drug Inspection, Western District.

<sup>2</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 72.

<sup>3</sup> *Z. Nahr. Genussm.*, 1900, 3: 1.

<sup>4</sup> *Ibid.*, 1901, 4: 145.

<sup>5</sup> *Ibid.*, 1913, 25: 717.

<sup>6</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 508.

dried eggs than does dry ether and accomplishes a practically complete recovery from noodles of the fat of the component materials obtained by the same method. The rigorous acid treatment, however, destroys the lipins and little phosphoric acid is found in the fat. Taylor and Nelson<sup>1</sup> found fat associated with starch not extracted by ether until after hydrolysis of the starch.

The lecithin-phosphoric acid recovery by the Juckenack method from noodles of known composition, in an investigation by the writer, page 84, was only 60 to 88 per cent of that of the ingredients. The Food Control Laboratory of the Bureau of Chemistry has made similar observations.

The available methods for fat and lecithin-phosphoric acid determinations being unsatisfactory, investigations were undertaken to devise better methods for determining all fatty substances, including lipins and lipin-phosphoric acid, in flours, alimentary pastes, noodles, and eggs, both liquid and dried. The method finally devised, which may be called a neutral extraction method, is described in the following paragraphs. The alcohol-ether extract determined by this method contains many substances besides neutral fats. The term lipoids is recommended to designate the substances so determined, as suggested by Rask and Phelps in an unpublished paper, in order to distinguish it from the ordinary ether extract. Under the general group of lipoids Czapek<sup>2</sup> includes neutral fats, phosphatides, phytosterol, pigments, waxes, and cerebrosides. The phosphoric acid of the extract is termed lipid-phosphoric acid.

## METHOD.

### *A.—As adapted to alimentary pastes, noodles, and flours.*

Grind the sample to pass an 80-mesh sieve. Place 10 grams of sample and 30 cc. of 70% alcohol in a 200 cc. nursing bottle and set in a water bath kept at 75°–80°C. Give the bottle a gentle rotary motion so as to moisten all of the particles with the alcohol. Heat for 15 minutes with frequent mixing by the same rotary motion. Add 55 cc. of 95% alcohol, stopper the bottle, and shake vigorously for 2 minutes. Add 85 cc. of ether, dried over sodium, and shake well for 5 minutes. The sample should now be in a fine state of division. Centrifuge just sufficiently to pack the sample lightly. Decant the liquid into a 250 cc. beaker containing some bits of broken porcelain, rinsing off the bottle neck with ether. Repeat the extraction of the sample with three successive 25 cc. portions of ether saturated with water, shaking one or two minutes each time, centrifuging, and decanting into the beaker containing the first extract. If the sample packs too firmly after centrifuging loosen it with a glass rod; should it become too dry to pack sufficiently to permit easy decantation, add a few drops of water to the ether. Evaporate the combined ether-alcohol extract to dryness on the steam bath; if necessary hasten the evaporation of the last drops of water by adding a little absolute alcohol. Dry the lipoids thus obtained in an oven at 100°C. for 45 minutes. Dissolve the dry lipoids in about 15 cc. of chloroform and filter. For

<sup>1</sup> *J. Am. Chem. Soc.*, 1920, 42: 1726.

<sup>2</sup> Czapek, Friedrich. *Biochemie der Pflanzen*, Vol. 1, 2nd ed., 1913, 709.

this filtration the following apparatus is recommended: In the top of a bell jar connected with a filter pump place the inner tube of a Knorr fat extraction apparatus (E. and A. No. 2810, 1920 Cat.), containing an asbestos pad which has been washed with alcohol and ether and dried. (The form of tube with a removable disk is preferred.) Filter the chloroform solution through this pad, receiving the filtrate in a weighed platinum dish. Carefully remove all traces of lipoids from the beaker by means of a chloroform wash bottle. The filtrate should be perfectly clear. Should the asbestos become clogged, hasten the filtration by gently rubbing the surface of the pad with a glass rod. Evaporate the chloroform off on the steam bath and dry to constant weight in the water oven (approximately 75 minutes). Report as lipoids. Saponify by warming with 5-10 cc. of 4 per cent alcoholic potassium hydroxide, evaporate to dryness, and char well in a furnace below red heat. Extract with nitric acid and determine phosphoric acid by the official volumetric method<sup>1</sup>, and report as lipid-phosphoric acid.

*B.—As adapted to dried powdered eggs.*

Use the filtering apparatus recommended in the preceding method for the filtration of the chloroform solution. Place 3 grams of the dry egg product in the Knorr extraction tube with an asbestos pad and wash with ether until most of the fat is removed. (It is advisable to stir the sample with a glass rod during this operation.) Collect the filtrate in a 250 cc. beaker. Evaporate the ether on the steam bath. By means of a wire, force the egg residue and asbestos pad, as one mass, out of the extraction tube into a small glass mortar. Carefully wash from the tube, and especially the tip, any adhering fat and add it to the main ethereal solution. Allow the ether in the egg residue to evaporate spontaneously. Add 2-3 grams of finely powdered calcium carbonate and rub to a fine powder with a glass pestle. (The grinding with calcium carbonate is to prevent lumping after treatment with 70 per cent alcohol.) Transfer the mixture to a 200 cc. nursing bottle. Rinse the mortar and pestle with ether and add to the ethereal fat solution. Add 20 cc. of 70 per cent alcohol and place in a water bath at 75°-80°C. Heat for 15 minutes, shaking frequently with a rotary motion. Add 35 cc. of 95% alcohol and shake 2 minutes. Add 55 cc. of dry ether and shake 5 minutes. Centrifuge and decant the alcohol-ether into the beaker containing the ether extract. Wash the egg residue with three 15 cc. portions of ether saturated with water. Dry the lipoids thus obtained for 1 hour in a water oven. Take up the dry lipoids in chloroform and filter into a platinum dish as indicated in Modification A. Evaporate off the chloroform and dry to constant weight in a water oven (approximately 75 minutes). Report as lipoids.

Determine the lipid-phosphoric acid according to Modification A. The official gravimetric method<sup>1</sup> in preference to the volumetric method is recommended for this determination because of the large quantity of phosphoric acid.

*C.—As adapted to liquid eggs.*

Mix sample with an egg beater and weigh out 10 grams into a 200 cc. nursing bottle; add 100 cc. of ether and shake the mixture well. Add five 5 cc. portions of 95 per cent alcohol, shaking after each addition. The gradual addition of alcohol with shaking coagulates the proteins in a very fine state. Centrifuge lightly and pour the ether-alcohol solution off into a 250 cc. beaker. Place on a steam bath. Shake the residue in the bottle free by a rotary motion with 25 cc. of 70 per cent alcohol and place in a water bath at 75°-80°C. for 15 minutes. Shake the mixture frequently with a

<sup>1</sup> Assoc. Official Agr. Chemists, Methods, 1920, 3.

rotary motion. Add 46 cc. of 95% alcohol and shake 2 minutes. Add 70 cc. of dry ether and shake 5 minutes. From here the procedure is the same as for dried eggs, Modification B.—“Centrifuge and decant the alcohol-ether”, etc.

### EXPERIMENTAL.

Detailed descriptions of the numerous experiments leading to the development of the proposed method will not be given. However, it was proved that one treatment with 30 cc. of 70 per cent alcohol for 15 minutes at 75°–80°C. gave just as high and concordant results as by varying the quantity of alcohol from 15–50 cc., or by treating twice with 30 cc. portions of the alcohol.

In Table 1 are given the analyses of three samples by different methods: The neutral extraction method, the Juckenack method for lecithin-phosphoric acid, and the unpublished method of Rask and Phelps.

TABLE 1.  
*Results showing averages of duplicate determinations.*

SUBSTANCE	NEUTRAL EXTRACTION METHOD		RASK AND PHELPS METHOD		JUCKENACK METHOD
	Lipoids	Lipoid $P_2O_5$	Lipoids	Lipoid $P_2O_5$	Lecithin $P_2O_5$
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Flour (Sample a).....	2.13	0.0531	1.84	0.0401	0.0293
Flour (Sample b).....	2.07	0.0461	1.82	0.0473	.....
Noodles (Sample c).....	4.13	0.0877	3.79	0.0765	0.0613

Sample (c) was again analyzed by the neutral extraction method, but the reagents used for the first extraction were those of the Rask-Phelps method. Ten grams of sample, 20 cc. of 95 per cent alcohol, 5 cc. of concentrated ammonium hydroxide, and 5 cc. of water were used. The results were: Lipoids, 3.79 per cent; lipoid-phosphoric acid, 0.0714 per cent. The lower results indicate, possibly, a decomposing action of ammonia on the lipins<sup>1</sup>.

TABLE 2.  
*Results obtained by the neutral extraction method.*

SUBSTANCE	LIPOIDS	LIPOID $P_2O_5$
	<i>per cent</i>	<i>per cent</i>
Dry Whole Egg (d).....	46.70	1.221
(Moisture-free basis).....	(49.7 )	(1.290)
Fresh whole egg (e).....	13.26	0.0404
(Moisture-free basis).....	(49.55)	(1.510)

<sup>1</sup> Mac Lean. Lecithin and Allied Substances—The Lipins, 1918, 33.

A sample of dried whole egg and one of fresh whole egg analyzed by the neutral extraction method gave the results shown in Table 2.

The percentage recovery, by the neutral extraction method, from a noodle of known composition (Sample f), of the lipoids and lipid-phosphoric acid of the ingredients, obtained by the same method, is shown in Table 3. The noodle was over one year old and contained 4.98 per cent egg solids, dry basis.

TABLE 3.

*Results showing percentage recovery from noodle (Sample f) by the neutral extraction method.*

(Moisture-free basis.)

	LIPOIDS	LIPOID $P_2O_5$
	<i>per cent</i>	<i>per cent</i>
Theory .....	4.80	0.1228
Actually recovered .....	4.67	0.0992
Percentage recovery .....	97.3	80.8

The recovery of only 80 per cent of lipid-phosphoric acid suggests two explanations: The extraction of the noodle was not complete or the lipins may have undergone partial decomposition either *during manufacture* of the noodle or during the period of storage. Jaeckle<sup>1</sup>, Ludwig<sup>2</sup>, and Nockmann<sup>3</sup> have noted an apparent decrease of the lecithin content of noodles during storage.

A fresh noodle (Sample i) was made up in a factory by the writer and analyzed; the component materials were also analyzed. This noodle was calculated to contain 5.17 per cent egg solids on the dry basis, from the factory formula. Table 4 presents the analyses.

TABLE 4.

*Results of analyses of noodles and ingredients.*

SAMPLE	NEUTRAL EXTRACTION METHOD			RASK-PHELPS METHOD	
	MOISTURE	LIPOIDS	LIPOID $P_2O_5$	LIPOIDS	LIPOID $P_2O_5$
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Dry Egg (g) .....	6.85	46.51	1.132	....	.....
	6.89	46.55	1.122	....	.....
Semolina (h) .....	12.99	2.48	0.0546	2.08	0.0501
	13.00	2.56	0.0580	2.08	0.0498
Noodle (i) .....	12.38	4.42	0.0947	4.11	0.0907
	12.39	4.49	0.0981	4.13	0.0953

<sup>1</sup> *Z. Nahr. Genussm.*, 1904, 7: 513.

<sup>2</sup> *Ibid.*, 1908, 15: 668.

<sup>3</sup> *Ibid.*, 1913, 25: 717.

Table 5 gives the percentage recovery, by the neutral extraction method, from the noodle (Sample i), of the lipoids and lipoid-phosphoric acid of the component materials.

TABLE 5.  
*Results showing percentage recovery from noodle (Sample i) by the neutral extraction method.*  
(Moisture-free basis.)

	LIPOIDS per cent	LIPOID $P_2O_5$ per cent
Theory.....	5.34	0.1240
Actually recovered.....	5.09	0.1100
Percentage recovery.....	95.3	88.7

The recovery of the lipoid-phosphoric acid is better than from the older sample of noodles, but it is still below theory.

During the preparation of a noodle, the flour and egg are in a moist condition for two to four days and are exposed to a temperature favorable to the activity of enzymes, molds, and bacteria. These agencies may cause a certain amount of decomposition of the lipins during this period, with a splitting off of some of the phosphoric or glycerol-phosphoric acid. The effect of the exposure of a noodle to moist air at room temperature was therefore studied.

Three 10-gram portions of the ground noodle (Sample i) were spread out on large watch glasses and placed on screen shelves in a large desiccator containing water. The samples were exposed to diffused light and water-saturated air at room temperature. Each portion was analyzed after different time intervals. The data are summarized in Table 6.

TABLE 6.  
*Effect of exposure of noodle to moist air*  
(neutral extraction method).

	LIPOIDS per cent	LIPOID $P_2O_5$ per cent
Original analysis.....	4.46	0.0964
After 3 days' exposure....	4.34	0.0844
After 5 days' exposure....	4.21	0.0742
After 6 days' exposure....	3.94	0.0641

Mold appeared on the sixth day.

A noodle, under the conditions of the preceding experiment, decreases in lipoids and lipoid-phosphoric acid content. The conditions under which a noodle is commercially made are quite similar to those met in this experiment. It is reasonable to conclude, therefore, that the lipins of a noodle decompose, more or less, during the manufacturing

process of mixing and drying. This fact may account for the recovery of only 90 per cent of the theoretical amount of lipid-phosphoric acid in the freshly made noodles. Similarly, Chapin and Powick<sup>1</sup> noted in liquid egg a continuous increase in the ratio between the inorganic and total phosphoric acid, in proportion as spoilage advanced.

In interpreting analyses of noodles, allowance should be made for recovery from the noodle of about 90 per cent only of the lipid-phosphoric acid of the ingredients, by this method. For noodles of long storage a greater allowance should probably be made.

#### SUMMARY.

A neutral extraction method is proposed for the determination of lipoids and lipid-phosphoric acid in flours, alimentary pastes, noodles, and eggs, both liquid and dry.

The essential features of the method are—

(1) The sample is in a fine state of division during the extraction. This is convenient and favors complete extraction.

(2) A temperature of 75°–80°C. is used to decompose lecitho-proteins.

(3) The sample particles are heated in 70 per cent alcohol, which makes them soft and easily penetrated by the solvents. The alcohol also dissolves the protein gliadin and aids permeation by the fat solvents.

(4) A neutral extractive is used to avoid possible decomposition of the lipins by acid or alkaline extraction media.

(5) The crude lipoids first extracted are purified by drying, redissolving in a water-free solvent, and filtering.

(6) The method permits the use of large samples, which may be increased, if desired, by using proportionally larger quantities of reagents.

The method yields results markedly higher in general than are obtained by other available methods.

Recovery of lipid-phosphoric acid from a noodle over *one year old* was 81 per cent of theory, and from a freshly made noodle, 89 per cent.

Experiment showed that a ground noodle exposed to moisture-saturated air at room temperature, fell off rather rapidly in lipid-phosphoric acid content. Noodles are exposed to similar conditions during manufacture.

The recovery of less than the theoretical content of lipid-phosphoric acid from a noodle by the method is very probably due to partial decomposition of the lipins during the mixing and drying of the noodles.

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<sup>1</sup> *J. Biol. Chem.*, 1915, 20: 97.



In calculating the egg solids in a noodle from its lipoid-phosphoric acid content, allowance should be made for the loss during its manufacture of some of the lipoid-phosphoric acid of the ingredients. It is suggested that the lipoid-phosphoric acid of the noodle be multiplied by 1.1 before making this calculation.

## THE BEHAVIOR OF PUMICE STONE DURING THE DEHYDRATION OF ORGANIC LIQUIDS.

By ARMIN SEIDENBERG (Chemical Laboratory, Department of Health, New York, N. Y.).

The pumice stone method for the dehydration of viscous organic liquids was first proposed by Weisberg<sup>1</sup>. It was later studied by Carr and Sanborn<sup>2</sup> and has been adopted as an official method by the Association of Official Agricultural Chemists<sup>3</sup>. Recently the writer<sup>4</sup> has used it for the determination of solids in comparison with a method depending upon the use of a gauze-dish consisting of a fine mesh wire platinum gauze with an area of 200 sq. cm. corrugated into 31 to 33 lateral ridges and compressed in this way into an area of  $8.5 \times 5.5$  cm. A study of the manner in which pumice stone affects organic residues distributed over it was made at the same time.

### METHOD OF WEIGHING.

All weighings were made by the single deflection method described by Brinton<sup>5</sup>. Gill and Simms<sup>6</sup> have used this method and obtained satisfactory results in weighing very small quantities of oil. Accurate weighings can be made rapidly by this method with only a partial swing to the right instead of the series of complete swings required in the usual method of weighing; at the same time fully as great a degree of accuracy can be maintained.

### WEIGHING BOTTLE.

The quantity of liquid for a determination was secured by weighing by difference out of a weighing bottle, which was a modified form of dropping bottle with a nozzle having a very small opening. In this way drops, averaging about  $\frac{1}{40}$  of a gram, were secured. The opening upon the back of the bottle was used to regulate the flow of the liquid as

<sup>1</sup> Bull. Assoc. Chem., France, 11: 524; U. S. Dept. Agr. Bur. Chem. Bull. 43: 272.

<sup>2</sup> U. S. Dept. Agr. Bur. Chem. Bull., 47: 134.

<sup>3</sup> Assoc. Official Agr. Chemists, *Methods*, 1920, 101.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1923, 15: 737.

<sup>5</sup> *J. Am. Chem. Soc.*, 1919, 41: 1151.

<sup>6</sup> *J. Ind. Eng. Chem.*, 1921, 13: 549.

is done from a pipet. After the delivery of the last drops any adhering film of liquid was removed from the nozzle by bringing it in direct contact with the dish into which the liquid had been placed.

#### VACUUM CHAMBER.

A wide-mouth, heavy glass jar resting upon its side in a Freas oven, which contained a cardboard shelf upon which the dishes could be placed, was used as a vacuum chamber. To carry off the moisture throughout the vacuum drying, air, which had bubbled through concentrated sulfuric acid, at the rate of about two bubbles per minute, was allowed to pass through the chamber. A manometer was attached to measure the vacuum, which usually equalled about 26–27 inches of mercury.

#### A. O. A. C. OFFICIAL METHOD.

According to the method of the Association of Official Agricultural Chemists<sup>1</sup> two layers of pumice stone—one a fine powder at the bottom, the other a layer of coarser particles—are used. In the case of levulose and other readily decomposable material, drying at 70°C. under vacuo is recommended; otherwise the drying is to be conducted in a water oven at the temperature of boiling water and under atmospheric pressure. Weighings are to be made at two-hour intervals in order to ascertain when dehydration has been completed. No mention is made of the manner of preparing the pumice before using. However, in the paper of Carr and Sanborn, already mentioned, and in the references to this subject by other writers such as Browne<sup>2</sup> and Davis<sup>3</sup> it is recommended that the pumice be prepared by first digesting with dilute sulfuric acid, washing with distilled water until the washings do not give an acid reaction, and then heating to redness. This in general is the method used by most chemists.

#### METHOD ADOPTED FOR PREPARING PUMICE STONE.

As it was found during the course of the work recorded in this paper that the method of preparing the pumice had an important bearing upon the results obtained in determining the solids, a somewhat different procedure was developed. After the pumice had been graded according to the size of the particles, it was digested for several days on the steam bath with dilute hydrochloric acid, washed first with water until the wash water was neutral to litmus, then with a dilute solution of ammonium hydroxide, and finally with water until a neutral reaction was obtained. After decanting as much water as possible, the pumice was

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 101.

<sup>2</sup> *Handbook of Sugar Analysis*, 1912 ed., 20.

<sup>3</sup> Allen. *Commercial Organic Analysis*, 4th ed. Vol. I, 67.

thoroughly dried by heating 4 to 5 days in an oven at a temperature of 130°–140°C. At this temperature hydrochloric acid, ammonia, and ammonium chloride are all volatile. After this treatment, the pumice was placed in a jar and allowed to remain under atmospheric conditions for several weeks before being used, when it was again dehydrated.

#### EFFECT OF TEMPERATURE AND PRESSURE UPON PUMICE STONE.

In order to ascertain in what manner and to what extent pumice itself is affected during the process of dehydration, a quantity of prepared pumice, about twice the amount usually used, was subjected for an extended period to varying conditions of temperature and pressure.

TABLE 1.

*Action of temperature on pumice heated in atmosphere at 100°C.*

(Weight of pumice: 37.4187 grams; combined original weight of platinum dish, pumice, and watch glass: 107.5151 grams.)

PERIOD OF HEATING	METHOD OF COOLING	WEIGHT	CHANGE IN WEIGHT
<i>hours</i>		<i>grams</i>	<i>gram</i>
24	Weighed immediately . . . . .	107.4540	−0.0611
	On balance 2 minutes . . . . .	107.4635	+0.0095
½	Desiccator—10 minutes . . . . .	107.4826	+0.0191
	On balance 2 minutes . . . . .	107.4868	+0.0042
24	Weighed immediately . . . . .	107.4548	−0.0320
	On balance 2 minutes . . . . .	107.4670	+0.0122
½	Weighed immediately . . . . .	107.4585	−.0085
1	Desiccator—10 minutes . . . . .	107.4825	+0.0240
	On balance 2 minutes . . . . .	107.4864	+0.0039
48	On balance 2 minutes . . . . .	107.4640	−.0224
1	Desiccator—10 minutes . . . . .	107.4870	+0.0230
	On balance 2 minutes . . . . .	107.4920	+0.0050
20	Weighed immediately . . . . .	107.4610	−.0310
72	Weighed immediately . . . . .	107.4560	−.0050
1	Desiccator—20 hours . . . . .	107.4937	+0.0377
4	Open (at room temp.) . . . . .	107.5010	+0.0073

#### Heated to redness 3 minutes.

½	Weighed immediately . . . . .	106.8750	−0.0260
24	Weighed immediately . . . . .	106.8830	+0.0080
1	Desiccator—10 minutes . . . . .	106.9056	+0.0226
	On balance 2 minutes . . . . .	106.9120	+0.0064
24	Desiccator—10 minutes . . . . .	106.9150	+0.0030
48	Desiccator—10 minutes . . . . .	106.9210	+0.0060
48	Desiccator—10 minutes . . . . .	106.9320	+0.0110
72	Desiccator—10 minutes . . . . .	106.9405	+0.0085
48	Desiccator—15 minutes . . . . .	106.9585	+0.0180
	On balance 10 minutes . . . . .	106.9675	+0.0090
60	Desiccator—15 minutes . . . . .	106.9946	+0.0201*
5	Desiccator—10 minutes . . . . .	106.9906	−0.0040*
96	Desiccator—10 minutes . . . . .	106.9942	+0.0036*
3	Desiccator—10 minutes . . . . .	106.9997	+0.0055†

\*Heated in atmosphere at 70°C.

†Heated in vacuum at 70°C.

First it may be noted (Table 1) that after the pumice has been heated, regardless of the temperature, there is a steady gain in weight from the moment the material is removed from the oven. The gain takes place even when the material is placed in a desiccator containing freshly ignited calcium chloride. The evidence indicates, therefore, that the gain in weight is not due exclusively to the adsorption of moisture. When the material was heated to redness over the Bunsen flame and subsequently placed for varying periods in the oven at temperatures ranging from 70°–100°C. under vacuo or under atmospheric pressure, a gain in weight extending over a period of weeks was noted.

#### EFFECT OF LIQUID UPON PUMICE STONE.

On evaporating a quantity of pure distilled water with pumice, it should be possible to regain the weight obtained before the addition of water. However, this was the case only when the pumice had been previously dehydrated under the same conditions as those under which evaporation was carried on and then only approximately (Column a, Table 2 and Columns a and b, Table 3) and after prolonged heating (about 10–11 hours). When the pumice, on the other hand, had been previously heated to redness (Column b, Table 2 and Column c, Table 3), there was first a loss of weight due to the evaporation of the major portion of the water and then a gain in weight that continued for 78 hours during which time weighings were made *without, however, regaining the original weight*. This holds whether evaporation is carried on under vacuo or at atmospheric pressure. In the case of the gauze-dish the removal of water is complete, and the original weight is again attained (at 100°C. in 1 hour) and after that closely maintained. Also the weight of the gauze-dish is not perceptibly affected by heating it to

TABLE 2.  
*Action of liquid on pumice and gauze-dish at 70°C. under vacuo.*

PERIOD OF HEATING AND PRESSURE	PUMICE		GAUZE-DISH
	a	b	c
Before heating . . . . .	31.8727	37.0945	27.4664
To redness . . . . .		36.7398	27.4662
4½ hours at 4 inch pressure . . . . .	31.8644		27.4663
2 hours at 2 inch pressure . . . . .	31.8643	36.7452	27.4663
Stood on balance 5 minutes . . . . .	31.8657	36.7482	27.4665
5 cc. distilled water added.			
5 hours at 2–5 inch . . . . .	33.1348	37.5514	27.4663
3 hours at 1.5–2 inch . . . . .	31.8652	36.7539	27.4662
3 hours at 4 inch . . . . .	31.8643	36.7533	27.4664
44 hours at atmospheric pressure . . . . .	31.8627	36.7594	27.4663

redness or by the varying conditions under which it is subsequently cooled and weighed.

From these results it is evident that the weight of the pumice is affected to a marked degree by conditions of temperature and pressure and by contact with a liquid. Indeed, it was found that its weight changed even during the process of weighing, and additional difficulties were also experienced in using a vacuum. In order to secure comparable results all material was cooled in a desiccator for a uniform period of exactly ten minutes before weighing. Weighings were made as rapidly as possible, the approximate weights first being placed upon the pans.

TABLE 3.  
*Action of liquid on pumice and gauze-dish at 100°C. and atmospheric pressure.*

PERIOD OF HEATING	PUMICE			GAUZE-DISH	SHALLOW DISH
	a	b	c	d	e
Before heating..	31.5921	32.4130	31.0607	27.4663	.....
To redness.....	.....	.....	30.7505	27.4663	20.4719
40 hours.....	31.5746	32.3957	.....	.....	.....
5 cc. distilled water added.					
1 hour.....	.....	.....	.....	27.4663	.....
1½ hours . . .	31.9400	33.0447	31.4097	27.4663	20.4716
1½ hours . . .	31.5780	32.3998	30.7630	27.4663	.....
1½ hours.....	31.5780	32.3994	30.7625	27.4665*	.....
1½ hours.....	31.5766	32.3988	30.7623	.....	.....
21 hours.....	31.5731	32.3952	30.7634	27.4662	.....
21 hours.....	31.5744	32.3942	30.7668	.....	.....
7 hours.....	31.5731	32.3950	30.7662	.....	.....
22 hours.....	31.5734	32.3953	30.7685	.....	.....

\*On balance 10 minutes.

#### EXPLANATION.

The<sup>1</sup> slow gain in weight occurring after evaporating solutions from pumice previously heated to redness has been generally ascribed to the action of the oxygen of the air, and for this reason Carr and Sanborn proposed evaporation in a vacuum. There is no evidence to support this view. In fact, as has been shown in the writer's previous paper<sup>1</sup> when a medium is used for distributing the liquid whose weight is not affected by the atmosphere, such as is the case with the gauze-dish, the sugar residues distributed over it are affected at any given temperature to exactly the same extent whether evaporation is carried at atmospheric pressure or in a vacuum. Similar results are reported by Hilts<sup>2</sup> in collaborative work on the dehydration of dried fruits containing

<sup>1</sup> *J. Ind. Eng. Chem.*, 1923, 15: 737

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 40.

levulose, for which no pumice or other material was used as the distributing medium. It was found that at any given temperature, after the period of moisture evaporation, a uniform rate of loss was found whether the evaporation was carried on in the air, in an atmosphere of hydrogen, or in a vacuum. The theory that the gain in weight is due to oxidation is therefore not supported by the facts. This gain in weight is to be noted only in the presence of material such as pumice or sand, which consists of a large number of small particles or which has many fine capillary openings; it increases with increasing pressure and with decreasing temperature. Some observers, such as Koydl<sup>1</sup> and Aikin<sup>2</sup>, have noted that the results secured on sugar solutions when sand was used as the distributing medium varied according to the average size of the sand particles. All these phenomena, producing variations in the weight of the pumice, can readily be understood as due to the property of adsorbing liquids and gases, commonly possessed by solid materials in a finely divided physical condition, and which are characteristic of the colloidal state. According to Bancroft<sup>3</sup> and others, materials such as this may be considered to be in a colloidal state.

#### EFFECT OF PUMICE STONE UPON SUGAR RESIDUES.

In the previous paper it was pointed out that when sugar residues were spread over pumice that had previously been heated to redness over the Bunsen flame, results were secured which, at temperatures of evaporation up to 100°C., remained approximately constant or in some instances showed a slight but continuous gain in weight. Usually the results were too high (in two series of determinations by 1.2 to 3.0 per cent of the actual dry residue), and unless the pumice had been prepared in one batch it was generally impossible to secure satisfactory checks. It will thus be seen that when "constant weights" were obtained they were fictitious and were the result of two counteracting sets of errors: one due to the gain in weight resulting from the adsorptive power of the pumice already referred to in this paper, and the other due to the loss in weight produced by the decomposition of the organic residues.

Radically different results were secured with sugar residues spread over pumice which had been dehydrated by being heated at the temperature at which the liquid was subsequently evaporated. Under these conditions sucrose residues, at the temperatures needed for complete evaporation of water, showed a continuous loss in weight. Where decidedly low temperatures were used the rate of loss due to decomposition was decreased, but it was not possible to expel completely all the moisture and to obtain a weight correctly indicating the solids present.

<sup>1</sup> *Centr. Zuckerind.*, 1909, 17: 1064.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1920, 12: 979.

<sup>3</sup> *Applied Colloid Chemistry*, 1st ed. 1921, 1.

Particularly was this the case with viscous material such as sucrose, which had a tendency to retain moisture, owing, perhaps, to the formation of minute solid films. These films, together with the moisture-retentive property of pumice, which increases with the decrease in temperature, tended to produce high results. When, on the other hand, a higher temperature was used, water could be expelled more thoroughly, but the loss in weight due to the decomposition of the organic matter was increased to a corresponding degree. This loss in weight is so decided and so continuous that it is not possible under these conditions to attain an approximate "constant weight" or a sharp end-point that will clearly differentiate the completion of the evaporation of the liquid from the decomposition of the solids.

In this way a "uniform rate of loss" occurs in the dry residue at a percentage of total solids above the correct percentage and continues to one indefinitely below it. While some authorities recommend that heating be continued until a "uniform rate of loss" is noted, it will be seen that this does not necessarily serve to indicate the correct percentage of solid matter.

Among the main factors affecting the rate of dehydration would appear to be quantity, concentration, and viscosity of liquid, manner of distribution of this liquid, physical condition, degree of dehydration and adsorptive power of distributing medium and pressure, and temperature used during dehydration. The rate of dehydration decreases greatly as the liquid becomes more concentrated. Some solutions which are viscous, such as those of sucrose, retain traces of moisture much more tenaciously than others of the same concentration, such as levulose. To some extent this may be due to the formation of solid films which mechanically enclose small quantities of moisture. It is therefore impossible to decide beforehand at the end of what period of time dehydration has been completed, particularly when a solution of unknown composition and concentration is dealt with. Evaporation for an arbitrary time can not for this reason be depended upon to yield the correct result. It is possible to secure dependable and correct results only where decomposition is negligible for a period of at least two and preferably three to four hours and where in any case the degree of loss due to this cause is decidedly less than that due to evaporation.

In one series of six determinations carried on at temperatures ranging from 57 to 117°C. and reported in the previous paper, after the correct solids as indicated by the specific gravity had been attained, the loss in weight, during a prolonged period of heating averaging 42 hours was approximately 0.04 per cent per hour; while in the case of parallel determinations carried on under exactly the same condition with the gauze-dish it was approximately 0.001 per cent per hour. Similar results were obtained on sucrose solutions distributed over sand (25 to

30 grams) previously dehydrated at 100°C. After the usual arbitrary period of heating at 100°C. for four to six hours the difference in results on four determinations run in parallel with the gauze-dish was 0.8 to 3.5 per cent of the actual solids present.

It appears from the distinct rate of loss of sucrose residues spread over pumice previously dehydrated at comparatively low temperatures that small traces of moisture are tenaciously held and can not be completely removed at these temperatures but can only be expelled by heating to redness. There is considerable evidence that decomposition of organic residues at these temperatures occurs, as is the case with certain chemical reactions, only in the presence of a trace of moisture, although, as is usual in these cases, it does not take place in a dilute solution. Thus the loss in weight of sugar residues when heated for a given time is less during one continuous period of heating than during an equal total of several shorter periods between which slight amounts of water are adsorbed during weighing. Charring and discoloration visible to the eye are much less on the gauze-dish which adsorbs practically no moisture, than on pumice, and they are less on pumice thoroughly heated to redness than on that not so heated. On several occasions it was noted that a very marked darkening in color took place in sugar residues distributed over pumice the moment the dish came in contact with the moisture of the atmosphere while being withdrawn from the oven. The conclusion that decomposition is greatly accelerated by the presence of slight quantities of adsorbed moisture may therefore be considered as well founded.

#### SUMMARY.

Pumice stone, or any substance consisting of small particles or having numerous fine capillary openings, has a greatly increased tendency to adsorb liquids and gases, particularly after being heated. The weight of material in this condition is affected to a marked degree by changes in temperature and pressure. It gains in weight after being heated while in a desiccator, and also during the process of weighing. For this reason also it readily adsorbs moisture from the atmosphere or from liquids spread over it. This adsorbed moisture is held very tenaciously and can only be removed by heating the pumice to redness.

It appears that the presence of this adsorbed moisture has a decisive effect in accelerating the decomposition of organic residues distributed over the pumice. When the pumice is heated to redness before being used and all the moisture thus expelled, an approximate constant weight may at times be obtained due to the balancing effect of two opposing errors. This constant weight may or may not be correct and checks can usually be secured only by preparing all the pumice used under identical conditions. Where the pumice is dehydrated at the com-



paratively low temperatures used for the evaporation of the liquid it is not possible to secure significant results that will indicate the true amount of solid matter present. If too low a temperature is used all the water is not expelled, particularly in the presence of viscous material. With higher temperatures it is not possible to secure a distinct end-point that will clearly distinguish between the loss due to the decomposition of the solid and that due to the evaporation of the liquid portion, and it is not possible to attain a significant "constant weight" that indicates the correct results.

## SECOND DAY.

### THURSDAY MORNING SESSION—*Continued.*

#### REPORT ON DETERMINATION OF PECTIN IN FRUIT AND FRUIT PRODUCTS.

By H. J. WICHMANN (U. S. Food and Drug Inspection Station,  
Denver, Colo.), *Referee.*

The most important event in connection with the work on the determination of pectin during the past year was the publication of an article<sup>1</sup>, by Marjory Harriotte Carré and Dorothy Haynes, entitled "The Estimation of Pectin as Calcium Pectate and the Application of this Method to the Determination of Soluble Pectin in Apples". The referee was extremely interested in this article. In it the authors question the completeness of the precipitation of pectin by strong alcohol. They make the following statement: "The lower limit of concentration at which pectin can be even partially precipitated has been found to be 0.06 per cent". This is an important statement and, if true, has a direct bearing on the methods for alcohol precipitate and pectic acid developed at the Denver Station and reported to the association last year<sup>2</sup>. The referee, therefore, changed his plans and limited his work this year to a critical investigation of this statement. Preliminary tests of the new method were made and the relationship between calcium pectate, as determined by Carré and Haynes, and "pectic acid", as determined by the method of Wichmann and Chernoff<sup>3</sup>, was ascertained.

In the Denver Station methods for alcohol precipitate and pectic acid, the pectin is precipitated from 20 cc. of aqueous solution by 200 cc. of 95 per cent alcohol. Six hundredths per cent of 20 grams is equivalent to 12 milligrams of pectin. The referee dissolved 5, 10 and 15 milligrams of a purified pectin in 20 cc. of water, added 200 cc. of 95 per cent alcohol and allowed the mixture to stand overnight. The next day a slight precipitate was noticeable in the 10- and 15-milligram samples, but none in the 5-milligram sample. When an attempt was made to filter these precipitates, the paper in every case became clogged with a colorless gelatinous mass. The pectin was so pure and in such a state of aggregation that it was almost invisible. Its index of refraction was almost the same as that of the alcohol solution. When the pectin was concentrated on the filter, it became plainly visible.

<sup>1</sup> *Biochem. J.*, 1922, 16: 60.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 34.

<sup>3</sup> *Ibid.*, 35.

It was impossible to make a quantitative recovery of the pectin owing to its extremely gelatinous character. The experiment was repeated, but 0.25 gram of pure sodium chloride was dissolved in the water before precipitation with alcohol. The electrolyte caused the pectin to precipitate in a flocculent form, and it was plainly visible in all three cases. In fact, a visible precipitate was obtained under these conditions with one milligram of pectin dissolved in 20 cc. of water and precipitated by 200 cc. of 95 per cent alcohol. Quantitative results with two different pectins were obtained as follows:

TABLE 1.  
*Quantitative results with two different pectins.*

	PECTIN ADDED			PECTIN RECOVERED		
	<i>mgs.</i>			<i>mgs.</i>		
Experiment 1	5	10	15	5.8	10.2	14.7
Experiment 2	5	10		5.8	10.4	

These experiments indicate that pectin, even in minute quantity, is insoluble in approximately 85 per cent alcohol, and may be quantitatively determined. If exceedingly pure, and the quantity is small, it may be invisible to the eye, in which case the addition of an electrolyte will cause it to flocculate and become plainly visible. The only conclusions that can be drawn from these experiments are that Carré and Haynes are in error, and that the accuracy of the Denver Station methods, in so far as the solubility of pectin in alcohol is concerned, can not be questioned.

The method adopted by Carré and Haynes for estimating pectin as calcium pectate is as follows:

A quantity of pectin is taken which will yield from 0.02 to 0.03 g. of calcium pectate; this is neutralized and then diluted to a volume such that after addition of all reagents the total volume measures about 500 cc. 100 cc. of N/10 NaOH are then added and the mixture is allowed to stand at least an hour, but preferably overnight. 50 cc. of N/1 acetic acid are then added, and after five minutes 50 cc. of M/1 calcium chloride. The mixture is then allowed to stand for an hour, after which it is boiled for a few minutes and filtered through a large fluted filter. If the precipitation has been properly carried out, filtration should take place very rapidly and subsequent washing should be easy. The washing is continued with boiling water until the filtrate is free from chloride, after which the precipitate is washed back into the beaker, boiled, and filtered again. It is then tested for chloride, and these processes are repeated until the filtrate from the boiled precipitate gives no indication of chloride with silver nitrate. It is then filtered into a small fluted filter, from which it can be transferred to a dish and finally to a Gooch crucible which has been previously dried at 100°. The precipitate is dried to constant weight at 100° which has been found to require about 12 hours.

A comparison of the above method with that of Wichmann and Chernoff for pectic acid is of interest. In both methods the pectin is

first saponified with dilute alkali. Carré and Haynes then acidify with acetic acid and precipitate the pectic acid as calcium pectate with calcium chloride. Wichmann and Chernoff precipitate the pectic acid with hydrochloric acid. Carré and Haynes must carefully remove all impurities, both organic and inorganic, from their precipitate before drying and weighing. This is not essential in the Wichmann-Chernoff method, in so far as inorganic ash material is concerned, because the pectic acid is determined by difference before and after ashing. Carré and Haynes are careful to recommend that a quantity of pectin be taken that will not yield more than 0.03 gram of calcium pectate, since a larger quantity will cause trouble in the washing and drying of the precipitate. Many times this quantity will cause no trouble with the Wichmann-Chernoff method, and therefore the percentage of error will be smaller. Acids natural or foreign to fruit products, glucose, gums, etc., cause no trouble with the Wichmann-Chernoff method, but may do so with the Carré-Haynes method, if they form calcium compounds insoluble in dilute acetic acid.

Some preliminary experiments were made to test the efficiency of the Carré-Haynes method, using as pure a pectin as it was possible to obtain. The conclusion, based on a limited number of experiments, is that it is possible to obtain good results if extreme care is exercised to give the precipitate of calcium pectate a thorough washing to remove all calcium chloride. It is difficult to remove inorganic impurities, such as calcium chloride, if once incorporated in the colloid. Consequently, the tendency, especially with those inexperienced in the method, is to obtain high results. With solutions containing unknown quantities of pectin, the analyst can only be sure of the accuracy of his results by determining the percentage of calcium in his calcium pectate. If this percentage is in the neighborhood of 7.6 (according to Carré and Haynes) his result is probably close to the truth, but if it is 8.0 per cent or over, it is too high.

The referee further tried the effect upon the determination of calcium pectate of adding 9 grams of sugar, 0.3 gram of citric or tartaric acid, or 0.2 cc. of 85 per cent sirupy phosphoric acid to 0.03 gram of pectin. These additions, in the quantities indicated, under the conditions of the method, appear to have had no appreciable effect. The principal reason for the tendency to obtain high results appears to be the incomplete removal of calcium chloride.

Time did not permit the determination of the effect of excessive washing, but with the complete removal of electrolytes the chances are that the calcium pectate might become partly soluble again and cause low results. The chief fault that the referee finds with the method is the difficulty of completely removing the calcium chloride and the consequent uncertainty of the results.

Soon after work on the two methods was begun, it became apparent that the pectic acids produced were not the same compounds. Pectin is a compound of high molecular weight and complex structure. Von Fellenberg<sup>1</sup> has shown that if pectin is treated with dilute alkali, methyl alcohol is split off. Tutin<sup>2</sup> believes that acetone is also split off. Chernoff<sup>3</sup>, of the Denver station, has shown that the treatment of sodium pectate with hydrochloric acid, in the cold, produces a gelatinous precipitate difficult to filter, and that boiling causes a flocculation of the precipitate and a further splitting off of a furfural forming compound. The pectic acid, as produced by the Wichmann-Chernoff method, is therefore a much simpler compound than the original pectin. The yield of pectic acid from pectins, obtained from various sources and manufactured by different methods, has varied from 50 to 75 per cent. This pectic acid appears to be a very stable compound and marks a definite stage in the degradation of pectin.

The calcium pectate, as determined by the Carré-Haynes method, is not so simple a compound as the pectic acid described. This is illustrated in Table 2. The results were obtained on a pectin prepared in the Denver laboratory.

TABLE 2.  
*Results obtained with pectin prepared in the Denver laboratory.*

	PECTIC ACID	
	Wichmann-Chernoff Method	Carré-Haynes Method
Pectin used, mgs. . . .	99.2	29.7
Pectic acid found, mgs.	60.3, 61.2	26.1
Pectic acid, per cent..	60.8, 61.6	87.8

The formula assigned to calcium pectate by Carré and Haynes<sup>4</sup> is  $C_{17}H_{22}O_{16}Ca$ , and theoretically it contains 7.66 per cent of calcium. This formula was employed in converting calcium pectate into pectic acid. It is evident, therefore, that a considerable difference exists in the two pectic acids. This difference is due to the furfural forming radical split off during the boiling with dilute hydrochloric acid in the Wichmann-Chernoff method and to another fraction, hitherto unknown, split off probably during the saponification of the pectin. This radical can be precipitated from neutral or acetic acid solution by calcium chloride and is soluble in hydrochloric acid. It is found in the filtrate from the Wichmann-Chernoff pectic acid precipitated either from hot or cold solution. In the pectins examined by the referee, it has

<sup>1</sup> *Biochem. Z.*, 1918, 85: 118.

<sup>2</sup> *Biochem. J.*, 1921, 15: 494.

<sup>3</sup> Unpublished data.

varied from 8 to 11 per cent of the original pectin. As calcium chloride does not form a precipitate with pectin itself, it is believed that it must be split off during the saponification. Under the conditions of the Carré-Haynes method it is included in the calcium pectate precipitate, which suggests that the calcium pectate is really a mixture. In fact, the calcium pectate of Carré and Haynes can be transformed into the pectic acid of Wichmann and Chernoff simply by boiling with 1 per cent hydrochloric acid, and this calcium compound can be precipitated in the neutralized filtrate.

The referee has precipitated calcium pectate and, without purification, converted it into pectic acid by boiling it with 1 per cent hydrochloric acid. Practically the same result as by the direct Wichmann-Chernoff method was obtained.

TABLE 3.

*Results of experiments to determine pectic acid.*

	<i>Experiment 1</i>	<i>Experiment 2</i>
	<i>mgs.</i>	<i>mgs.</i>
Quantity of pectin.....	100.0	98.7
Pectic acid (Wichmann-Chernoff method).....	75.6	61.5
Pectic acid by preliminary precipitation as calcium pectate, subsequent boiling with 1% HCl solution in dilute NaOH and reprecipitation with HCl.....	76.2	60.4

These experiments suggest that the preliminary separation of pectin by alcohol in the Wichmann-Chernoff method for pectic acid may be omitted and a separation by calcium chloride substituted. There might be distinct advantages in this.

This work of the referee is preliminary in nature, but it demonstrates that care must be exercised in the future to distinguish between the calcium pectate of Carré and Haynes and the "pectic acid" of Wichmann and Chernoff, for they do not correspond in composition. The calcium pectate may be a mixture of two compounds; if not, it certainly is an intermediate compound between pectin and pectic acid. The referee is not prepared at this time to state that the calcium pectate method has any advantages over the method reported last year. It is considered that more work is required to clear up uncertain points.

#### SUMMARY.

It has been shown that pectin is very insoluble in 80 to 90 per cent alcohol. If in quantity less than 10 milligrams in 220 cc. of alcohol, and if very pure, it may be invisible. Electrolytes will cause it to flocculate and become amenable to quantitative determination.

The Carré-Haynes method for calcium pectate yields accurate results only when great care is used in the washing of the precipitate. There

is a tendency towards high results, owing to the difficulty of removing calcium chloride from the colloidal precipitate. Limited quantities of sugar, tartaric, citric and phosphoric acids do not cause high results under the conditions of the method.

Calcium pectate and the pectic acid of Wichmann and Chernoff do not correspond in composition. There is some evidence that calcium pectate is a mixture. It can be transformed into pectic acid by boiling with dilute hydrochloric acid. If not a mixture it is an intermediate compound between pectin and pectic acid.

#### RECOMMENDATION.

It is recommended that further work be done on the method of Carré and Haynes for the determination of calcium pectate and on the pectic acid method of Wichmann and Chernoff, in an effort to shed light on the composition of pectin.

### REPORT ON DETERMINATION OF MOISTURE IN DRIED FRUIT.

By R. W. HILTS (U. S. Food and Drug Inspection Station, U. S. Appraiser's Building, San Francisco, Calif.), *Referee*.

The work on the determination of moisture in dried fruit has followed closely the recommendations adopted by the association in 1921<sup>1</sup>. Further collaborative study was made of the proposed official vacuum oven method for the determination of moisture in all dried fruits and of the tentative water oven method for the determination of moisture in dried apples only. Some additional experimental work was done. An attempt was also made to adapt to dried fruit the calcium carbide method for determining moisture. The referee makes acknowledgment to J. C. Palmer, of the San Francisco Station of the Bureau of Chemistry, who performed the experimental work herein described.

For the collaborative studies, large samples of dried apricots, peaches, and apples, in condition as packed, were allowed to stand in closed vessels for several days to equalize the moisture and were then passed three times through a meat chopper, being mixed thoroughly after each grinding. Portions were immediately placed in glass-stoppered bottles which were paraffined. Sets of these samples were submitted to the collaborators, together with copies of the vacuum oven method for dried fruits in general and the water oven method for dried apples only, in the exact form recommended in last year's report<sup>2</sup>. The collaborators

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 48.

<sup>2</sup> *Ibid.*, 40.

were instructed to determine moisture in all three samples by the vacuum method and in the apples by the water oven method in addition. To prevent possible evaporation it was specified that the entire sample should not be removed from the bottles, but that suitable portions for each determination should be removed by a spatula or spoon, after the upper portion of the material in the bottle had been rejected. Additional instructions to collaborators were as follows:

Report the reading of the vacuum gage, if the oven is provided with the usual gage reading in inches of mercury, and also the uncorrected barometer reading for the same day. Specify the type of vacuum oven used, *i. e.*, whether water jacketed or electrically heated. In case of the water oven report the actual oven temperature as indicated by a thermometer whose bulb is placed near the dishes. The water oven should have at least one vent on top to secure ventilation. If your equipment differed in any manner from the above, describe in detail.

The collaborators' results are summarized in Table 1.

#### DISCUSSION.

The pressures given for the vacuum ovens were obtained by deducting the readings of the vacuum gage from the prevailing uncorrected barometer readings, and on account of the inaccuracy of these gages they are only approximate. With three exceptions the vacuum ovens used were of the cylindrical water-jacketed gas-heated type with perforated metal shelves. McIntire and Dill used a Freas electrically heated vacuum oven with inner vacuum chamber, and Twining used a Mojonnier oven, which is essentially an electric hot plate enclosed in a vacuum chamber. As stated last year, the accurate determination of moisture in these products is difficult, and minor differences always occur in the rather elaborate equipment employed. For these reasons very close agreement can not be expected, and it is considered that the results for the vacuum oven method are on the whole reasonably satisfactory. The results on dried apples are very good indeed, but those of Boudreaux by the vacuum method are out of line—being low—which is accounted for by the fact that he was unable to secure as high a vacuum as specified in the method. If this analyst's results are not considered, out of the remaining 84 results reported, 44, or 52 per cent, are within 0.5 per cent of the average.

The referee desires to emphasize two important points mentioned last year in connection with vacuum oven drying: (1) The desirability of placing the samples in metal dishes resting directly on metal shelves in contact with the walls of the oven so as to permit rapid conduction of heat to the sample; and (2) the necessity of providing a means for displacing the water vapor by a current of dry air. The referee doubts whether the vacuum oven method can be materially improved and recommends its adoption as official for all dried fruits, with a certain modification to be discussed later.



TABLE 1.

*Results of collaborators on moisture determination in dried fruit.*

ANALYST	APRICOTS	PEACHES	APPLES		AVERAGE PRESSURE IN VACUUM OVEN	TEMPERATURE OF WATER OVEN
	Vacuum	Vacuum	Vacuum	Water Oven		
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>inches of mercury</i>	<i>°C.</i>
C. W. Harrison, Baltimore, Md.	23.60 23.42	22.70 22.52	21.28 21.28	21.99 22.43	2.0 or less	98-100*
C. H. Hickey, Boston, Mass.	23.77 24.01	23.00 23.14	21.76 21.70	21.81 21.79	1.45	96
L. W. Ferris, Buffalo, N. Y.	24.21 24.28	23.61 23.56	21.90 21.87	23.08 23.04	2.0	99.5
C. A. Roach, Chicago, Ill.	22.88 22.77	22.17 22.06	21.39 21.30	22.84 22.95	4.0	96.5†
M. L. Hitchcock, Cincinnati, O.	22.44 22.48	21.45 21.45	20.65 20.58	22.16 22.20	0.82	97.5†
H. J. Wichmann, Denver, Colo.	24.11 24.19	23.26 23.12	21.65 21.88	22.23 22.24	0.10	95
E. C. Boudreaux, New Orleans, La.	19.04 18.48	19.68 18.81	20.55 20.22	21.40 21.57	25	95-96
D. B. Scott, New York, N. Y.	23.71 23.75	22.84 22.78	21.51 21.44	22.13 22.06	1.85	97
J. C. Palmer, San Francisco, Calif.	24.05 24.18	23.25 23.22	22.00 21.97	22.35 22.39	1.5	97.5
J. Callaway, Jr., Savannah, Ga.	23.98 24.06	22.88 22.97	21.71 21.72	22.41 22.49	0.14	96
D. H. McIntire, Seattle, Wash.	23.76 23.78	22.81 22.76	21.53 21.49	22.26 22.47	0.64	98
D. B. Dill, Seattle, Wash.	23.84 23.86	22.80 22.86	21.56 21.53	22.39 22.58	0.64	98
A. L. Burns, St. Louis, Mo.	24.19 24.21	23.39 23.34	21.94 21.96	22.35 22.19	1.66	100*
J. I. Palmore, Washington, D. C.	21.82 22.14	22.06 22.30	21.45 21.58	22.16 22.20	3.0	97
F. E. Twining, Fresno, Calif.	20.33 19.94 20.11	22.53 21.60 21.27	..... ..... .....	21.89 22.17 22.64	2.8	99.5
Maximum.....	24.28	23.61	22.00	23.08		
Minimum†.....	19.94	21.27	20.58	21.40		
Average‡.....	23.24	22.68	21.56	22.25		

\*Used electrically heated ovens instead of water ovens.

†Used double-wall steam-heated ovens instead of water ovens.

‡Excluding results of Boudreaux by vacuum method. See discussion.

The results obtained by the collaborators on apples by the water oven method are in reasonably good agreement. Out of 31 results reported, 23, or 74 per cent, are within 0.5 per cent of the average. The range of variation is very much less than was the case with pears, peaches, and apricots by the water oven method in last year's work, confirming the statement then made that this method appeared to give reasonably consistent results with apples but not with other dried fruits. In this report the average of the results by the water oven method is shown to be 0.69 per cent higher than by the vacuum method. However, the agreement between the two methods can not be judged by results on a single sample. As stated in last year's report, the San Francisco Station, in 1920, made comparative determinations by both methods, in practically the form here described, on 52 samples of apples of 10 grams each, and the average for the water oven method was exactly 0.1 per cent higher than by the vacuum oven method. In only seven of these samples was the difference greater than 0.5 per cent, and it was usually very much less. A rapid method of this sort, requiring only simple equipment, is of great practical value to food control officials and especially to manufacturers for factory control purposes, and it is again recommended that this method for dried apples only be adopted as tentative. The referee recommends, however, a slight change in the wording, which will permit the use of steam-jacketed or electric ovens, as well as water ovens, providing the temperature does not exceed that of boiling water or fall below 96°C. and is definitely and uniformly maintained. Unfortunately, this is not possible with all electric ovens. A note as to ventilation of the oven has also been inserted in the method.

In last year's report it was stated that results by the vacuum oven, using 5- or 10-gram samples, were found to be practically the same, the differences being within the limits of experimental error. A few additional experiments on this point were made this year, with results as shown in Table 2.

TABLE 2.

*Results showing influence of size of sample on vacuum method for moisture.*

SIZE OF SAMPLE	APRICOTS	PEACHES
<i>grams</i>	<i>per cent</i>	<i>per cent</i>
10	24.05 24.18	23.25 23.22
5	24.04 23.98	23.03 23.14

The results in Table 2 confirm the statement previously made. The use of a 10-gram sample in the vacuum method was recommended

simply because it was felt that the larger sample would be more likely to be representative in the case of all the fruits except apples and raisins, on account of the difficulty of grinding and thoroughly mixing the material. However, there is no reason why 5 grams will not give as reliable results as 10 grams if the fruit is well ground and mixed, and an appropriate change in the wording of the method is recommended so as to permit the use of samples from 5 to 10 grams in weight.

In last year's report a brief statement was made to the effect that previous experience of the San Francisco Station in determining moisture in raisins by the vacuum method had shown that it was necessary to use a 5-gram sample with an absorbent in order to obtain uniform and consistent results. To verify this, additional experiments were made upon a sample of seeded raisins by three different modifications, using 5- and 10-gram samples without any absorbent, and also 5-gram samples dried on asbestos. In the last modification, 5 grams of sample were weighed into a metal dish containing 2 grams of finely divided asbestos previously dried and weighed with it. Hot water was added, and the whole was thoroughly mixed, evaporated on the water bath just to dryness, and then placed in the vacuum oven. The drying was completed as in the general vacuum method. The results are shown in Table 3.

TABLE 3.  
*Results of determination of moisture in seeded raisins by vacuum method.*

10-GRAM SAMPLE, NO ASBESTOS	5-GRAM SAMPLE, NO ASBESTOS	5-GRAM SAMPLE, WITH 2 GRAMS OF ASBESTOS
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
14.96	15.28	16.33
15.06	15.41	16.39

The figures in Table 3 confirm the previous experiments and indicate that considerably higher results are obtained with the absorbent than without it. It is probable that the very high percentage of sugar in raisins accounts for this fact and makes the drying of such fruits more difficult. Last year's experiments did not indicate any advantage in the use of asbestos with pears, peaches, and apricots. The referee believes that this difference in behavior is quite important and is recommending an addition to the wording of the vacuum oven method to provide for the use of asbestos as an absorbent in the case of raisins, currants, and other fruits similarly high in sugar.

The experimental work on the calcium carbide method for determining moisture was undertaken not so much in the hope that it might be suitable for general use but rather with the idea that since it depended upon a totally different principle from the drying methods, it might

serve as a check, or absolute method, to prove the accuracy of the moisture results obtained in the vacuum oven. In these experiments the apparatus used was exactly the same form as that recommended by McNeil<sup>1</sup>, including an auxiliary metal container for acetylene, holding about 1200 cc., which would permit the use of 5-gram samples of dried fruit. A solution saturated with both sodium chloride and acetylene was used in the measuring buret and auxiliary container. Many difficulties were encountered. As it seemed practically impossible to obtain an intimate mixture and complete reaction between the powdered calcium carbide and the dried fruit, either alone or when mixed with sand, it was deemed necessary to use some liquid miscible with water in the reaction flask. Absolute alcohol was chosen as the most promising. With water alone reasonably consistent results were obtained, one gram yielding approximately 580 cc. of acetylene under standard conditions. With water and alcohol, however, inconsistent results were obtained. Some difficulty was experienced in obtaining a complete reaction, since the alcohol could not be heated above its boiling point. The reaction with dried apples and carbide in the presence of absolute alcohol also appeared to be slow, and periods of heating up to 45 minutes were necessary. Some of the sources of error are the difficulty in securing complete reaction, the solubility of acetylene in absolute alcohol and in water, and the vapor tension of alcohol. One or two results in fair agreement with the vacuum oven method on a sample of apples were obtained, but the analysts felt so little confidence in the method that further experiments were discontinued. The referee believes that it involves too many sources of error to make it valuable as an absolute method.

#### RECOMMENDATIONS.

It is recommended—

(1) That the following method for the determination of moisture in all dried fruits by drying in vacuo be adopted as official:

##### *General method for all dried fruits.*

Weigh 5-10 grams of sample into a metal dish about 8.5 cm. in diameter, provided with a cover, breaking down any large lumps. Dry in vacuo at 70°C. for 12 hours at as low a pressure as possible, not to exceed 4 inches (100 mm.) of mercury. During the drying admit to the oven a slow current of air, about 2 bubbles per second, dried by bubbling through concentrated sulfuric acid. The metal dish must be placed in direct contact with the metal shelf of the oven. Replace cover, cool in a desiccator, and weigh. Disregard any temporary drop of oven temperature which may occur during the fore part of the drying period owing to rapid evaporation of water. With raisins and fruit similarly rich in sugar use about 5 grams of sample and about 2 grams of finely divided asbestos dried with the dish. Moisten with hot water, mix sample and asbestos thoroughly, evaporate on the water bath barely to dryness, and complete drying as above.

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<sup>1</sup> Bur. Chemistry Circ. 97: 1912.

(2) That the following method for the determination of moisture in dried apples only be adopted as tentative:

*Method for dried apples only.*

Weigh 5–10 grams of sample into a metal dish about 8.5 cm. in diameter, provided with a cover, breaking down any large lumps, and dry for 4 hours in an oven at the temperature of boiling water. Replace cover, cool in a desiccator, and weigh. Place dishes on shelves and not on oven bottom. The oven should have a vent on top to secure ventilation, and the temperature should not be below 96°C.

No report was made by the Referee on Canned Foods.

*President Veitch:* These meetings would lose much of their charm and value to us if we did not expect to see and hear the Honorary President of this association, Dr. Harvey Washington Wiley.

### ADDRESS BY DR. WILEY

MR. PRESIDENT, MEMBERS OF THE ASSOCIATION, LADIES AND GENTLEMEN:

I reciprocate the sentiment which has just been expressed by your president, namely, that of mutuality. I should not think this was a proper occasion unless I had the privilege of being here. I believe I hold the unique distinction of never having missed a meeting of this association. I hope I can continue to hold that distinction for several hundred years to come, as I know of no event in my public life to which I look forward with more interest than this annual assemblage. I believe I am the one poet, of world-wide repute, who has devoted a volume to the songs of this association<sup>1</sup>. I wish you would sing more of them than you do.

I think it is appropriate that I should speak today for a short time upon the theme which is uppermost in the minds of the citizens of Washington at this time—cancer week. I have had the opportunity of making several addresses during the week, and I hope it will not be considered out of place to say just a few words here.

It is peculiarly appropriate that one should address a company of chemists on the subject of cancer, because one of the remedial agents which is now in the public mind, as well as in the medical mind, has been provided by the activities of chemists. I doubt whether any informed physician in the country ever thinks of cancer without associating it with the idea of radium. Although radium is not regarded as either a certain preventive or a certain cure for this disease, it can not be denied that it has some therapeutic value. In a disease which seems to be so resistant to every kind of curative treatment, any agent that gives any reasonable hope of help must be regarded with great con-

<sup>1</sup> Song book of Agricultural Chemist, illustrated by Coffin. Privately printed 1903.

sideration. So, the chemist stands very close to the doctor in this Cancer Week which is being observed all over the country.

I am not going to tell you the symptoms of cancer or of any of the methods which may be provided for its elimination. I can only say that if there be any hope at all for one afflicted with this dreadful disease, it is in its early ascertainment. If you wait too long, there is no remedial agent known to medical science which can be relied upon as at all hopeful. I was particularly struck with this last June at the meeting of the Associated Harvard Clubs of the United States, at Cambridge and Boston. One of my classmates seemed less lively than I had ever known him. He is a very distinguished man and for many years has been on the governing board of the university, and is still there. As a member of that governing board, it is his duty to come out at commencement time, and especially when the associated clubs of the country are meeting in Boston. He had always been a hearty eater, which is very characteristic of Harvard people. In the banquet hall, I happened to sit near the head of the table. I sometimes have the opportunity of sitting at the head of the table at banquets, but I much prefer the other positions where I can better hear what is said. I noticed my friend left the table in the midst of the banquet and did not return. The next day I happened to see him at Nantasket Beach and I chided him with having lost his pep. He said: "Come over here, I want to speak to you". I went. He opened his mouth and put out his tongue and there I discovered a full-grown cancer, already involving the greater part of this organ, and inside of it I saw a little glass tube. When I asked him what that was, he said: "That is a particle of radium which my physician has imbedded in my tongue as the only possible hope of arresting this disease. It is probably too late".

Here is a man in the midst of his career, about eight years younger than I. I had the distinction of being older than anybody else in the class. He should have many years yet of useful activity. I am afraid to write to him, because I fear the answer—if he is still alive—will be unfavorable<sup>1</sup>. This case brings home to me in the person of a dear friend and classmate the enormity of the suffering and the minimum hope of rescue from this great disease. When I pick up a newspaper or magazine and see an advertisement of a cancer cure—a sure cure or your money back, if the undertaker will let you send it back—and the picture of a cancer with roots with the advertisement of this certain cure, I am overwhelmed with hate and disdain for such lying, mischievous, and deceptive advertising. In the first place no cancer ever had a root—there are no such things as cancer roots; in the second place, medicine is absolutely useless; and in the third place, such advertising

<sup>1</sup> Nine months later. I have just seen my classmate. He is on his way from San Francisco, his home, to attend his fiftieth anniversary. He thinks his tongue is entirely well.

induces in the person suffering from this disease a hope which postpones any application for real medical attention. And these magazines boast of spreading the truth and light among our people! I read in one of the papers this morning an article by one of our distinguished citizens, saying that the newspapers of Washington are the cleanest in the United States in regard to the exclusion of misleading advertisements. I did not have time to look them all over, but I found fifteen lying advertisements before I had finished with one paper in this city. Therefore, I say one of the great enemies of mankind is the lying advertisement of cancer cure, and that is one thing that has not been stressed in this city during this week.

I do not want to frighten you into believing you have a cancer. I want to say that cancer is never produced by belief. Nerve shocks are sometimes produced by belief, which reduces the vitality of the system, but no disease, infectious or otherwise, was ever produced by belief, and no disease of any kind, except a disease that never existed, was ever cured by belief.

The normal attitude of the individual towards cancer is this: to have a suspicion of every sore of every kind, of every mole or lump, or of any irritated portion of the epithelium, because most cancers are epithelial. While an irritated condition of the skin may not be and probably is not cancer, it is always worth while to give your attention—not only your attention as a healer of yourself, which is most unprofitable—but such attention as will lead you to consult your physician in regard to the nature of the irritation. Cancer is a chronic disease and is produced, if we know its cause at all, not so much by a violent wound as it is by continued irritation. You smokers will be glad to know that there are eighteen cases of cancer on the lips, on the tongue, and on the throat of men where there is one in women. Why is this? Every doctor will tell you that it is the smoking habit of men. Now that women are striving after equality, they are learning to smoke, and they will gradually achieve the same distinction in epithelioma that men have already attained.

That one organ of the body that is common to men and women, the stomach, is of all organs the most subject to cancer because it is of all organs the most constantly and continuously irritated by improper diet and especially by improper temperatures of the diet. That part of the lining of the stomach through which a very cold or a very hot drink passes is usually the part of the mucous membrane in which cancer has its place. If you will read a poem, in "Beverages and Their Adulteration", you will see a poetic description of one of the great causes of cancer of the stomach. I have the permission of the author to quote it:

“Full many a man, both young and old,  
Has gone to his sarcophagus,  
By pouring water icy cold  
A down his hot œsophagus”.

Avoid extremes of temperature in your food. Avoid the eating of substances which irritate the mucous membrane of the stomach, and thus preserve that organ from its very frequent attack of cancer.

What I think about most on an occasion of this kind is the progress our science has made since we last met. I will confess that with the partial obliteration of my vision it has been difficult to keep up with the progress in chemistry, and naturally I do not try to keep up with its progress in every department. Even if I had as good eyes as I have had, it would be almost impossible. However, I do try to keep abreast with what is going on in my particular line of agricultural chemistry, and just now when I am endeavoring to write the third edition of the first volume of “Principles and Practice of Agricultural Analysis”, my attention has been called to another very great step in the progress in chemistry, and I want to say a few words about that today.

Our ideas of the nature of matter have undergone most remarkable revolutionary changes in my lifetime. When I first studied chemistry it was the old chemistry of Liebig and Lavoisier and the old masters. What they knew was a mouthful. We hardly realize what progress those old masters made, not only in the practice of chemistry but in its theories. Among other things, we learned Prout’s theory of the atom. According to Prout, the atom was composed of an indivisible particle of an elementary nature, to which he gave the name protile. Prout assumed that as atoms were made up of increments of like matter—namely, atoms of hydrogen, which was taken as unity—their atomic weights ought to be whole numbers. That was Prout’s original hypothesis, but as we learned to determine atomic weights with greater precision, we found that many were not whole numbers. Some were nearly whole numbers and might be regarded as such by the chemists, but others were decidedly not whole numbers. These distinctions were not due, evidently, to lack of scientific accuracy in the determination, and so Prout’s hypothesis did not account for existing phenomena in a manner to be generally acceptable. But now, what have we discovered in the history of the evolution of the atom? In the first place, the idea of the atom is inconceivable, as no finite mind can conceive of a particle of matter so small that it is incapable of further division. Literally, an atom is an uncutable substance, that is, from its Greek derivation. But still the word atom perhaps will remain, though the conception of it, as has already been shown in the books you have read, has undergone a wide evolution. We are taught that the atom is made up of two kinds



or manifestations of matter, a push and a pull. There are only two kinds of matter in the whole cosmic universe. And when you can conceive that the diameter of one of these particles may be represented by 2.7 micromillimeters multiplied by 10 to the minus 13th power, that is about as small as you can conceive. Yet we can conceive of that mass without doing violence to our imagination, but it is so minute that no microscope can ever bring it into view, so it is intangible to the optic nerve. Therefore, you do not have to pay any tax on it unless you live in the District of Columbia. The tax collector here can tax the intangible. This kind of matter has been named, and the names are very generally accepted. From Prout's name of protile came proton, the positive particle. The negative particles are called electrons. That is the modern theory of the atom. For a long time we disregarded the corpuscular character of the atom. I remember having made considerable fun, some 40 or 50 years ago, of a philosopher by the name of A. Wilford Hall who upheld this theory of the atom. I guess he was about right, and that I was wrong, for these particles that constitute the atom are said to be really particles of matter. They can be projected into space when the atom particle disintegrates. Therefore, they must be something more than a push and a pull. They are called "pellates" in the new nomenclature, when they push. Electrons are the other kind of matter. They are pellates among themselves but when they come near together, one proton or two protons and one electron, they become tractates when they pull. It is the old idea of electrical attraction and repulsion expressed in a different way. Then there is great discontent in the atoms and molecules of many substances. They are not satisfied. If we regard the union of protons and electrons as a matrimonial union—the married men can understand what that means—there is a great deal of domestic infelicity, and we know what that means, too. This is followed by divorces without going to the courts. These atoms degenerate and disappear and throw out particles called alpha particles. Oh! what would we do without the Greek alphabet? We would not be able to name anything we did not know anything about. The alpha particle is said to be composed of four protons and two electrons and it is a nucleus of an atom. Now, I understand that the protons are the male elements and the electrons are the female elements, because they are always on the outside and want to leave home, except those that are united in the nucleus; there are always more protons in a nucleus than electrons and if the number of electrons in the nucleus increases, then the discontent and domestic infelicity increase to the extent that these particles are ejected from the atom, thrown with tremendous velocity through space equal almost to the velocity of light and as they go they are imbued with the idea that they ought to get remarried. That is quite human; in fact the history

of the atom as it is presented today is the history of humanity—discontent, dissatisfaction, seeking something better and farther away. I believe after all that probably the Bible is the best book on chemistry. As I have said once before in speaking of colloidal chemistry, it is the first book on colloidal chemistry ever published, and when the Bible says, "Male and female created He them", God did not think so much of the Adam and Eve we think of as He thought of the protons and electrons, and it fits in exactly with this new theory of matter. The new alpha particle consists of four protons and two electrons and as the alpha particle is projected into space it wants to become settled again. After I got married, I was asked to address a Parent-Teachers Association. I went. An amiable teacher said that they had been trying to get Dr. Wiley for a long time and had been unsuccessful, but now that he was married and settled down, they had been able to get him. I appreciated the teacher's compliment, but I said, "The first thing I had to do when I got married was not to settle down, but to settle up". So when this alpha particle is projected into space, it seeks more electrons to become stable, and then it becomes that very useful substance we are seeking to produce in great quantity, known as helium. The helium, which we now find with natural gas or water under the earth, is forming constantly whenever an atom displaces an alpha particle, which is projected into space. Now, this bombardment has many other functions, as we know. It is probable that it forms the healing element in radium by projecting this particle into space so that it penetrates the human organism and strikes the cells of the cancer, destroying their vitality. But this remedial agent, while useful in cancer in its early stages, is frequently very dangerous and produces burns and sores by unscientific handling. But the atom also throws out a beta particle. Here comes the Greek alphabet again. It is an electron pure and simple that is being thrown out as a bombarding agent, but it throws out another thing which is not a particle. It is an emanation. They call it a gamma ray. Hurrah again for the alphabet. So there are three kinds of energy, you may say, in this atom which nobody has ever seen or felt except as the result of bombardment, that is when it disintegrates, and it does constantly disintegrate and does throw out two particles of corpuscular matter—a particle of negative electricity, the beta particle, and a positive particle in the case of the alpha particle. This emanation is probably identical with the X-ray emanation, a force and not a particle.

This is the present conception of the constitution of matter. When I read of the wonderful work which has been adduced to explain this theory and which does coincide with all the requirements of the theory, I have an additional admiration for the chemist's calling. It is certainly a triumph of our great science to think that this wonderful theory,

which is probably correct, can be determined by analytical and experimental ways, which show that these things are always taking place, that these particles are actually flowing from this disintegrated atom, and that this bombardment actually occurs. I have not time here, if I could by memory repeat these determinations, but they are thoroughly scientific, easily repeated by those who have the skill, and they give evidence which is quite convincing. But I never attach myself to a theory so strongly that I can not break away. When I accept a theory, it is only a tenable theory as long as it explains the phenomena we are observing.

Another thing attached to this theory is extremely interesting. It supports Prout's old theory that all matter is alike, that the whole universe is composed solely of protons and electrons and that they are the same wherever they exist, one and indivisible. In that sense the proton of gold is the same as the proton of hydrogen, and that of chlorine the same as of sodium, and the electrons in the nucleus are always the same wherever they exist. Then the question comes, "How do they explain the wonderful difference in the chemical and physical properties of matter"? That is yet to be solved but the nucleus theory seems to be pretty well established.

That reminds me of the nucleus theory of the evolution of living beings. This poem was not written by W. J. Bryan. It is a song supposed to be sung by a protozoan of some kind.

I was a rhizopod with protoplasmic cells  
 I had a little nucleus and I had nothing else,  
 Since then a man I've grown by evolution's power,  
 But Oh! my little nucleus, I miss thee every hour.

I have taken sufficient time to relate some ideas and impressions of what we consider to be the great progress of the science to which we belong. As I was listening to our president's paper, I was wondering, after all these years of activity, what there could be for this association to do, but when I heard him say that there was no uniformity nor likeness of activity in regard to that one little thing, the determination of calcium requirements of the soil, I felt that the task before this association is still just as great as it was at the beginning. In other words, the field of knowledge is so broad, compared with that which we know, that no matter how rapidly we progress or what distinguished attainments we reach in this science, the unknown will always be before us, offering still endless fields and opportunities for investigation. So, there is no end to the good which this association may do. It is boundless in its activities and in its field of endeavor, and so I want to say that we should never be satisfied to think that we have learned it all but keep that humble attribute which is the characteristic of a scien-

tific mind, perfect humility even in the attainment of the great progress which we have made. That is the reason why the really scientific man is never proud of what has been accomplished but always bows in humility before the Great Unknown—whether he calls it God or Jehovah or Nature or by another name.

*President Veitch:* As always, Dr. Wiley has given us something else to think about.

Service might almost be said to be the second name of this association. It is rare that those who are served have called the chemist to the high places in government. No member of this association has served his people more effectively, more successfully, nor had his service more appreciated by his people than has Senator Ladd, and it is with great pleasure that we now have the opportunity to hear from him and to congratulate him upon the fact that his services to his people have had this recognition.

#### ADDRESS BY SENATOR E. F. LADD.

MR. PRESIDENT, FELLOW CHEMISTS AND FRIENDS:

I assure you that I still like to call myself a chemist, although I may have wandered far afield during the past few years. I feel more at home today, as I look back into the faces of those I have known, and many I have never met before, than I have ever felt among politicians. I hope I may continue to have your sympathy and support, for there is no greater field in my mind than that of chemistry, and no official association in the past has rendered such great service to the people of this country and other countries as well, as has this association.

In the early days, this association was made up of a few of the straggling chemists of this country, banded together and organized in order to enable them to get better results and do more efficient work in the examination and control of fertilizers. Gradually that work has expanded and grown until today this organization has become powerful. It is the organization that is looked upon throughout the world as the leader in formulating methods, and I feel that its work is going to broaden in the years to come. You will be called into new fields to carry on investigations along regulatory lines. I hope, among other things, that in the near future national laws may be enacted along several lines that will throw a new responsibility upon the regulatory chemist and afford new opportunity for research work and new fields of endeavor in our educational institutions and agricultural colleges. I believe the time is not far distant when we shall have the banner of truth unfurled, and you will be called upon to take an active part. We shall have a paint law and a varnish law that will be for the best interests of the people and, in the end, for the best interests of the manufacturers themselves.

Your work today is very different from what it was 38 years ago when this association was organized. I think that was the year, 1884, when I took my first position in the field of chemistry. I was fortunate in being associated with a man for whom I have great respect, Dr. S. M. Babcock. I was with him four years. Those four years were to me the most profitable I ever spent in chemical work.

It was not my good fortune to be at the first meeting of this association, but I have been present at most of the meetings that have been held since, and I am glad to say that the man who organized this association, who has guided it so largely through its early career, is still actively with us and has given a splendid address to stimulate activity on our part.

In those earlier days people had even more faith, perhaps, in the chemist than they have today. I well recalled as I was sitting here thinking, how I went into my laboratory one morning and found a man with a jar of water. He said, "I have come all the way up here, 150 miles, to bring you this jar of water, and I want you to examine it and see if I have discovered coal". In reply to a few questions, he gave the following explanation: "As we finished digging a well and it was getting dark, we struck a black vein down some 40 feet in the earth at the bottom of the well. So we left it till morning, and this morning the well was half filled with water. I took this jar and filled it and brought it up for you to examine and see if we have a coal bin down there". There are many laughable instances of that kind as well as many opportunities for real service to the people.

I notice on your program today that you still have the same subject unsolved that we contended with years ago, the old question of crude fiber. It was my pleasure one year to spend considerable time trying to find out something more in regard to crude fiber. I do not know whether you are any farther along than I was at that time. I did an enormous amount of work without making very much progress, but every year a little has been done on this subject, until in the end a great deal has been accomplished.

I did not come here today to make any extended remarks. I came for the purpose of meeting with the chemists I have known in the past and to show my good will and my respect for the great calling of chemistry and for those who have continued in the work. I will repeat that I believe there is no greater field or opportunity for a young man today than the field of chemistry, but one thing has always annoyed me in my duties, which have not been confined to the teaching of chemistry and to research. That is the way expert testimony is frequently handled when it is necessary for the scientist to go into court. If I could impress upon every chemist the need for reform in this one thing, expert testimony, I should think I had rendered a good service to the cause of chemistry and to the people of this country.

Unfortunately, we too frequently allow the lawyer to determine for us what we shall give as evidence, and in doing so we often bring discredit upon the profession. I will give one illustration only, but I might name scores of instances that have come under my observation. A well-known chemist had been the first to condemn a certain practice in this country—condemn it in strong terms; therefore I called upon him to get his support and secure his services in a court case, involving the same principles. He said he would come for \$500, and \$50 a day. That was not unreasonable but I told him that unfortunately I was not in a position to give that, as I was paying the expense myself. He said, "It does not make any difference to me. I will take the other side. They want me and will pay me that amount". I said "Good-bye". Up to that time I had had great respect for him, but I lost much of it when he made that statement.

Very frequently the chemist lets the attorney shape the question to meet the attorney's ideas and in doing so he only presents a half truth, which brings confusion and misunderstanding. It leads the jury to be uncertain, and it leads to wrong decisions. Now, if the chemist would insist that he formulate his own questions and give his own answers and do it in advance, there would be a much better presentation of the case and the evidence. The time should come when the courts will use some other means to select the experts to give the testimony in important cases, for you can always find men ready to take either side. There are cases where such a condition may possibly be necessary, but in the majority of cases it is not so.

I recall a case where three of America's most prominent chemists, for one thousand dollars each, allowed their attorneys to do that very thing. The chemists would be known to all of you owing to their prominence. After their testimony had been given, the testimony was taken on the other side, and it was my privilege—or misfortune—to be the chemist to testify on that side. I had a long and severe battle with the attorneys before they would allow me to testify in my own way, but finally they yielded. I wrote the questions in advance and I wrote the answers, and the testimony was given as I asked to have it given. I had no better chance to win than the other side, but when the time for rebuttal came the three chemists admitted that they had not given all the facts that they should have given and asked for an opportunity to revise their testimony. It was granted, and while the comment of the court was not in the language that I shall use, nevertheless in substance it meant that the three experts gave their testimony, and after I had given mine they found that it was necessary to and did revise their testimony, but mine remained unchallenged. What happened in reality was that the testimony of the three experts of America was discredited, and that of an obscure chemist was accepted, although

more than half of my testimony was on their side of the case. This was simply because I had insisted that the questions and the answers, as I was going to give them, should be written in advance. The attorney did not want my testimony given in that way but if I have ever been impressed with any one thing, all through my somewhat busy life in court work, it is with the necessity of giving the expert witness an opportunity to present all the facts and insist that he do so. If there is not sufficient merit to warrant this, then there is not sufficient merit in it for you to be a party. There is too much biased expert testimony before the courts of this country. I have thrown this thought out as one of the things that have impressed me in our court work. It is an important matter and worth considering. I think the feeling throughout the country is that the time is coming soon when we shall be forced to adopt some other system of providing for expert testimony before commissions or for court purposes. I think an association of this kind can render a service by emphasizing the need for such a change.

I came here simply to extend, by my presence, my good will to this association and its members and to meet those with whom I was associated in years past. I thank you for this opportunity of being with you.

*President Veitch:* It is a great pleasure to the association to hear from Senator Ladd. I think his remarks have shown us clearly why he has such a standing and is so addressed.

## SECOND DAY.

### THURSDAY AFTERNOON SESSION.

#### REPORT ON CEREAL FOODS.

By C. H. BAILEY (Agricultural Experiment Station, St. Paul,  
Minn.), *Referee*.

Collaborative studies on cereal foods have been confined, during the past year, to methods for (a) the determination of fats in baked cereal products, and (b) the determination of chlorine in the fats of raw flour.

Two samples of dried and finely ground baked products were distributed to several collaborators. Sample D was ordinary white bread; Sample E was "soda biscuit" or crackers. The method prescribed for the determination of their fat content was essentially like the method devised by C. R. Smith, which gave the most satisfactory results in the collaborative studies of 1921. It has been published as Method II in the proceedings of the 1921 convention<sup>1</sup>.

Ten collaborators reported the results of fat determinations, employing the referee's method, with the results shown in Table 1. In several instances, two or more determinations were reported, in which event the results were averaged.

TABLE 1.  
*Collaborative results on the determination of fat in bread and cracker samples.*

COLLABORATOR	SAMPLE A BREAD	SAMPLE B CRACKERS
	<i>per cent</i>	<i>per cent</i>
C. E. Goodrich, Bureau of Chemistry, Washington, D. C. . .	3.45	10.25
Ruth Buchanan, Bureau of Chemistry, Washington, D. C. .	3.50	10.45
R. L. Rutledge, Bureau of Chemistry, Washington, D. C. . .	3.52	10.22
E. L. Tague, Agricultural Experiment Station, Manhattan, Kans. . . . .	3.09	9.68
Janet Ullrich, W. P. Tanner-Gross & Co., New York City .	3.45	9.75
M. J. Blish, Agricultural Experiment Station, Lincoln, Neb.	2.98	10.04
W. C. Luckow, American Institute of Baking, Chicago, Ill.	3.32	10.23
B. R. Jacobs, National Cereal Products Laboratory, Wash- ington, D. C. . . . .	3.88	10.35
Emily Grewe, Federal Mill & Elevator Co., Lockport, N. Y.	3.32	10.36
G. R. Taylor, Agricultural Experiment Station, St. Paul, Minn. . . . .	3.32	10.71

The results are in good agreement, as was true the preceding year. No material criticism of the method was offered by any of the collabora-

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 61.



tors. It is, accordingly, recommended that this method for the determination of fat in baked cereal products be made official.

#### DETERMINATION OF CHLORINE.

Chlorine in the fat of three raw flours was determined by five collaborators. Sample A was natural or unbleached hard spring wheat straight flour; B was bleached with chlorine at the rate of approximately  $2\frac{1}{2}$  ounces of chlorine per 6 barrels of flour; while C was presumably treated with 3 ounces of chlorine per 6 barrels of flour. The chlorine additions were controlled by means of one of the appliances ordinarily employed in flour milling. It is highly probable, however, that under the working conditions there was comparatively little difference in the dosage of chlorine in the two instances. The treatment was approximately that given in commercial practice in milling hard spring wheat.

The method prescribed by the referee for the determination of chlorine in the fat of flour differed but slightly from Method No. 1, outlined by O. S. Rask<sup>1</sup>, associate referee on cereal foods in 1921. Experience of certain collaborators in 1921 indicated definitely the undesirability of using a nickel dish in charring the extracted fat in contact with alkali. It was accordingly specified that the fat be charred in platinum, a detail which made collaboration impossible on the part of a number of chemists who did not possess platinum dishes of sufficient capacity.

The details of the method follow:

##### *Method for the determination of chlorine in the fats of flour.*

Weigh 75 grams of the flour into a cork-stoppered bottle and add from a pipet 150 cc. of petroleum ether (fractionated at 60°–100°C.). Stopper tightly and shake vigorously for about 1 minute. Allow to stand for 1 hour, again shake until the flour particles are in suspension, and then set aside overnight. Shake once more to suspend the flour particles, allow to settle for a few minutes, and filter through a dry, folded filter. (The funnel should be covered with a watch glass to reduce evaporation during filtration.) Pipet 50 cc. of the filtrate into a platinum dish of about 80 cc. capacity. If a platinum dish of this size is not available, evaporate the 50 cc. of filtrate to a small volume in a porcelain evaporating dish over a steam bath, and carefully transfer the fatty concentrate to a small platinum dish, washing out the last traces of fat with several small portions of petroleum ether. Add 5 cc. of a 4% potassium hydroxide (or sodium hydroxide) solution and evaporate to dryness on a steam bath. Char carefully in a muffle at low redness. Extract the charred mass with 2 successive 20 cc. portions of dilute nitric acid (1 part nitric acid to 3 parts water), being careful to avoid mechanical losses due to evolution of carbon dioxide. Filter these extracts through a 7 cm. quantitative filter paper into a 300 cc. flask. Then extract the mass two or three times with water, filtering each portion through the same 7 cm. paper. Return this filter paper to the platinum dish containing the charred residue, and ignite to a white ash in a

<sup>1</sup> J. Assoc. Official Agr. Chemists, 1922, 6: 68.

muffle. Dissolve the ash in 5% nitric acid solution, and add the solution to the filtrate previously obtained. Neutralize the acidity with a slight excess of dry calcium carbonate. Add 5 cc. of the chromate indicator solution and titrate with the standard silver nitrate solution, made by dissolving 4.791 grams of silver nitrate in water and diluting to 1 liter. Each cc. is equivalent to 1 mg. of chlorine. Prepare a blank containing the quantity of all reagents used in the determination. Since calcium carbonate commonly contains appreciable quantities of chlorides, a definite, weighed quantity of this reagent should be employed in each determination and the same quantity used in the blank. From 2.0 to 2.5 grams are sufficient. Correct for the quantity of silver nitrate solution necessary to give in the blank, with 5 cc. of the chromate solution, the shade obtained at the end of the titration of the sample. Report results in terms of parts per million of chlorine.

Since the quantity of chlorine involved in such determinations is relatively small, care should be taken to insure that the laboratory atmosphere is as free from chlorine as possible. The blank determination should be conducted at the same time and under the same conditions as the other determinations.

The results of these chlorine determinations are given in Table 2.

TABLE 2.

*Collaborative results on the determination of chlorine in the fat of raw flour.*

COLLABORATOR	NATURAL FLOUR A	BLEACHED FLOURS	
		B	C
	Parts per million of flour	Parts per million of flour	Parts per million of flour
C. E. Goodrich.....	2	94	92
Ruth Buchanan.....	0	96	90
M. J. Blish.....	0	88	52
G. R. Taylor.....	31	104	148
W. C. Luckow.....	16	188	164

Luckow reported difficulty in titrating the solution of chlorides to a distinct end-point with silver nitrate. He employed the Volhard method with the following results, in parts of chlorine (in the fat) per million of flour:

A	B	C
4	79	52
2	80	52.8
5.3	77.2	51.6

These values were lower, in the case of the bleached flours, than those reported by other collaborators in titrating with silver nitrate.

The agreement in the five reports is only fair. It appears, however, that each analyst was able to distinguish sharply between natural or unbleached flour and flour treated with chlorine, as in usual commercial

practice. Apparently further study should be made of the method before adopting it as official but, owing to its usefulness, the referee recommends that it be adopted as a tentative method, and that a further study be made of other methods available for the determination of chlorine in flour.

The official methods of the association for the analysis of cereal foods<sup>1</sup>, Paragraphs 1-7, have been criticized by certain organizations of cereal chemists on the ground that they are not sufficiently specific and detailed. The referee accordingly suggests that certain amplifications of these methods be considered which do not of necessity modify their principles with a view toward amending them later. The additions which the referee recommends for consideration are as follows:

Amplify the method for the determination of moisture under XIV, 1, to read as follows:

Dry 2 grams of flour in a tared metal dish about 40 cm. in diameter by 25 cm. high, and provided with a tight fitting cover, to constant weight in a vacuum oven at a pressure not to exceed 5 cm. of mercury, and at a temperature of 100°C. Cool the dish in a desiccator, and weigh immediately after the dish and contents reach the temperature of the air in the laboratory.

Amplify the official method for the determination of ash under XIV, 2, to read as follows:

Ignite a crucible, and when cooled, weigh, and rapidly weigh into it 5 grams of the flour. Ignite in a muffle at approximately 550°C., taking care that no portion of the muffle becomes sufficiently hot to fuse the ash. A light-gray, fluffy ash should result. Cool the crucible and contents in a desiccator, and weigh immediately after it reaches the temperature of the laboratory air.

Amplify the statement under the description of the method for the determination of crude protein, XIV, 7, to provide that the percentage of nitrogen in wheat, as well as in flour, shall be multiplied by 5.7 to obtain the percentage of protein. Some confusion appears to exist with regard to reporting the percentage of crude protein in wheat, and it seems logical to employ the same factor in this case as in the case of flour. The wheat kernel is largely endosperm, and hence its chief proteins are gliadin and glutenin, which contain nitrogen in such proportions as to justify the use of the factor  $N \times 5.7$ .

The referee suggests that these amplifications be made the subject of discussion during the next year, particularly between the Referee on Cereal Foods and the appropriate committee of the American Association of Cereal Chemists. If no objections are made to these amplifications of methods, already official, or if other details are agreed upon, the unanimous consent of the Association of Official Agricultural Chemists

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<sup>1</sup> *Assoc. Official Agr. Chemists, Methods, 1920, 167.*

might properly be asked at the 1923 convention to such modifications as will render the official methods more acceptable to cereal chemists. It is probable that other cereal methods, official and tentative, might be subjected to similar treatment during the next year or two.

#### RECOMMENDATIONS.

It is recommended—

- (1) That the tentative method adopted at the 1921 meeting for the determination of fat in baked cereal products be made official.
- (2) That the method for the determination of chlorine in bleached flour, as given in this report, be adopted as a tentative method.
- (3) That further studies be made of the methods for the determination of chlorine in bleached flour.
- (4) That the official methods for the analysis of cereal food be amplified as specified in this report.

#### REPORT ON LIMIT OF ACCURACY IN THE DETERMINATION OF SMALL AMOUNTS OF ALCOHOL IN BEERS.

By B. G. HARTMANN (U. S. Food and Drug Inspection Station, Chicago, Ill.), *Referee*.

No experimental work has been done. The specific gravity and refractometer methods for determining the alcohol content in beers<sup>1</sup> are believed to be satisfactory. It is, however, suggested that the text be changed to provide for a higher concentration in the distillate to be employed for the final determinations. Your referee believes that if the distillation is made from 100 to 50, instead of from 100 to 100 without dilution or neutralization, accurate results will be obtained. Attention is called to the referee's report for 1920, in which it is shown that extremely close checks may be obtained when using the specific gravity and refractometer methods on samples of near beer.

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<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 173.

## REPORT ON VINEGARS.

By W. C. GEAGLEY (Department of Agriculture, Lansing,  
Mich.), *Referee*.

In accordance with recommendations of the referees in 1919-1921, the work for 1922 was carried out along the following lines:

A review of the literature with reference to glycerol, solids, and fixed acids was made, with the idea in mind that new methods or modifications could be worked out to overcome the objections which have been raised against the present official methods<sup>1</sup>.

## GLYCEROL.

The referee was unable to find a method which, after a try-out in the laboratory, offered any apparent advantage over the present method for glycerol or that gave sufficient promise to warrant the expenditure of much time in collaborative study. It is a question with many workers on vinegars whether it would be desirable at this time to change in any manner the procedure for the glycerol determination.

## TOTAL SOLIDS.

The methods for total solids and fixed acids present somewhat the same aspect.

It has been shown by a number of analysts and confirmed in the referee's laboratory that solids which are comparable can be obtained if the details of the official method are followed exactly, *especially in regard to the size and style of the dish used*.

## FIXED ACIDS.

In view of the fact that the so-called "fixed acids" have been shown to consist largely of lactic rather than malic acid, it would appear that the designation "non-volatile acids" would be a more accurate heading for this determination. Further, it would appear that instead of calculating as "malic acid", it would be better to report as "non-volatile acid" in terms of acetic acid, for the reason that this determination is made principally for the purpose of calculating the volatile acids present.

A study of the present methods having shown that several other determinations are in more urgent need of study than those for glycerol, total solids, or fixed acids, the views of several analysts working on vinegar were secured, and from these the following recommendations were compiled.

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<sup>1</sup> Assoc. Official Agr. Chemists, *Methods*, 1920, 191.

## RECOMMENDATIONS.

It is recommended—

(1) That for the purpose of clarifying the records Paragraph 1<sup>1</sup>, "Physical Examination", be adopted as an official method. This is the second recommendation for the adoption of the determination as official, the first having been made in 1919. Its status has apparently been overlooked by subsequent referees.

(2) That the methods for the determination of alcohol, reducing sugars, polarization, and color be studied by the referee during the coming year.

(3) That methods for the determination of sulfates and barium be considered by the referee during the coming year.

No report was made by the Referee on Meat Products.

No report was made by the Referee on the Separation of Meat Proteins.

## REPORT ON GELATIN.

By C. R. SMITH (Bureau of Chemistry, Washington, D. C.),  
*Associate Referee.*

Methods for the analysis of gelatin have been submitted to the association by the referee and published in *The Journal*<sup>2</sup>. These methods have been in use for a number of years in many government and commercial laboratories, but some of them have not been studied by the association.

The determination of heavy metals in gelatin is necessarily connected with the work of the Referee on Metals in Foods. Methods of treatment of the gelatin preliminary to the metal analysis present an excuse for this work being conducted by the Referee on Gelatin.

A sample of gelatin was sent out to the collaborators with instructions to examine for copper and zinc by the following methods:

*Copper*<sup>3</sup>.

Hydrolize 50 grams of gelatin with 150 cc. of dilute hydrochloric acid, 1 to 3, as directed under arsenic, heating about 2 hours on the steam bath. To facilitate filtration and separation from zinc and iron later, use the phosphoric acid or compound and magnesia mixture as before. Precipitate with hydrogen sulfide in a slightly ammoniacal solution. Allow the precipitate to settle, filter, and wash with 5% ammonium chloride solution saturated with hydrogen sulfide. Dissolve off the zinc and iron sul-

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 191.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 343.

<sup>3</sup> *Ibid.*, 344.

fides, magnesium phosphate, etc., in 75 cc. of dilute hydrochloric acid (4%) saturated with hydrogen sulfide. Digest filter and copper sulfide with 4 cc. of concentrated sulfuric acid and sufficient nitric acid until the residue is perfectly colorless and fuming freely. Take up with water and determine copper by titrating with 0.01N sodium thiosulfate, as directed in the official method<sup>1</sup>.

### Zinc.

Determine the zinc in the filtrate from the copper determination as directed both in the official method<sup>2</sup> and below:

Boil the filtrate to expel all hydrogen sulfide. Make the solution strongly ammoniacal and then acidify with 15 cc. of 50% formic acid. Filter off any insoluble matter such as alumina, etc., while hot, and then pass in a rapid stream of hydrogen sulfide for 10 minutes. Warm the solution 15 minutes on the steam bath, remove, and allow to stand for 30 minutes before filtration. Filter the zinc sulfide on a carefully prepared Gooch crucible with a very gentle suction, washing with 2% ammonium thiocyanate. Dry and ignite at the highest temperature of a Bunsen burner. Cool and weigh the zinc oxide.

The results are given in the following table. The figures refer to parts per million.

*Results of determinations of copper and zinc in one sample of gelatin.*

ANALYST	COPPER	ZINC		REMARKS
		A. O. A. C. Method	Formic Acid Method	
C. R. McKee, U. S. Glue Co., Milwaukee, Wis.	26.0	308.5	305.3	Obtained 17 parts copper by a colorimetric method.
A. L. Rawlins, United Chemical & Organic Products Co., Hammond, Ind.	25.9	370.0	448.0	Copper 25.0 by own method and 428 parts zinc.
	23.1	392.0	369.0	
Swift & Co., Chicago, Ill.	19.0	302.0	336.0	
C. R. Smith.	28.5	....	314.6	
J. B. Cohen, Atlantic Gelatine Co., Woburn, Mass.	27.0	260.0	230.0	

This sample had been previously analyzed by different methods, unknown to the referee, in commercial laboratories. The results, which follow, expressed as parts per million, show wide divergence and prove the need of careful attention to uniform methods such as have been submitted by this association.

<sup>1</sup> Assoc. Official Agr. Chemists, *Methods*, 1920, 79.

<sup>2</sup> *Ibid.*, 151.

LABORATORY	COPPER	ZINC
A	16.0	40
B	135.0	318
C	21.6	286
D	19.5	283

A. E. Paul, of the Chicago Laboratory, submitted methods for manganese and mercury in addition to those for lead, copper, and zinc. While the referee does not think that time can be spared by the association for studying the analysis for such unusual elements as mercury and manganese (or chromium), the analyst should bear in mind the possibility of their presence when examining samples suspected to be glue.

#### COMMENTS.

Swift and Co. reported difficulty in titrating copper with 0.01N thiosulfate. Their usual method is to burn 50 grams after moistening with 10 to 12 cc. of concentrated sulfuric acid. The copper is obtained as sulfide, dissolved, and later determined colorimetrically with potassium ferrocyanide. Later work on the same sample showed 53 and 57 parts by one analyst and 46 parts by a second.

The United Chemical and Organic Products Co. reported using a hydrolysis method combined with sulfide precipitation and later colorimetric estimation with potassium ferrocyanide.

The referee notes that the laboratories in the Central West are using a variety of methods. Most of the laboratories in the East are using the methods essentially as sent out. The referee's experience has shown that the copper method is very satisfactory when used by analysts familiar with it. It is probable that the principal difficulty is in the use of starch in titrating small amounts of iodine. It is recommended that analysts avoid the use of starch and titrate in small volume. Traces of iron should be removed by filtration when the solution is ammoniacal, and then the excess of ammonia removed so as to avoid all but small amounts of ammonium acetate.

#### RECOMMENDATIONS.

It is recommended—

(1) That the method for the determination of copper be continued as a tentative method.

(2) That further study be made of zinc methods and of the alternative method for copper<sup>1</sup>.

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 345.



## REPORT ON SPICES AND OTHER CONDIMENTS.

By ARTHUR E. PAUL (U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.), *Referee*.

## SALAD DRESSING.

The need for definite and satisfactory methods for the analysis of salad dressings becomes more urgent with the increase in manufacture and variety. Although the composition of the salad dressings on the market varies greatly, a few ingredients are common to all of them, and for these the present methods are more or less satisfactory. It was believed that it would be desirable, during the present year, to prepare a simple form of dressing, from known weights of the most common ingredients, and subject it to careful collaborative examination by the methods which are now available, with a view to making the satisfactory methods official and modifying those that do not produce acceptable results.

## SAMPLE.

A mixture was made, according to the following formula, and with the given percentage composition:

	GRAMS	PER CENT
Cottonseed oil	298	8.26
Peanut oil	596	16.52
Olive oil	2086	57.84
Vinegar	311	8.62
Mustard	22	0.61
Sugar	18	0.50
Salt	40	1.11
12 egg yolks	231	6.40
Boric acid	5	0.14
	3607	100.00

The ingredients were mixed as thoroughly as possible in an endeavor to produce a permanent emulsion, but there appears to have been some separation in one instance. However, collaborators were requested to mix their samples thoroughly before weighing out portions for analysis.

## METHODS.

The methods for the preparation of the sample and the determination of total solids, reducing sugars before and after inversion, sucrose, total acid, volatile acid, oil, and lecithin  $P_2O_5$ , essentially as formulated by H. A. Lepper, which have been published in *The Journal*<sup>1</sup>, were submitted to collaborators.

Juckenack<sup>2</sup> gives the following average values for average-sized eggs:

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 248.

<sup>2</sup> *Z. Nahr. Genussm.*, 1900, 3: 11.

WEIGHT OF MATERIAL	DRY SUBSTANCE	TOTAL $P_2O_5$	LECITHIN $P_2O_5$
<i>grams</i>	<i>grams</i>	<i>gram</i>	<i>gram</i>
Yolk.....16	7.835	0.2046	0.1316
White....31	4.540	0.0097	0.0000
Whole egg.47	12.375	0.2143	0.1316

By using these figures the approximate egg content of a dressing can be calculated from the lecithin  $P_2O_5$  content.

#### REPORT BY COLLABORATORS.

It is regretted that only four collaborators reported on the samples. They were the following: Raymond Hertwig, San Francisco Station; John H. Bornmann, Chicago Station; W. S. Hubbard, New York Station; and M. L. Hitchcock, Cincinnati Station.

The results obtained, as well as the corresponding approximate theoretical figures, are given in the table.

*Collaborative results on determination of composition of salad dressings.*

METHODS	APPROXIMATE COMPOSITION	HERTWIG	BORNMANN	HITCHCOCK	HUBBARD
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Total solids . . . . .	88.19	88.98	89.75	88.89	89.05
Reducing sugars before inversion . .	0.04	0.15	0.16	0.05	0.06
Reducing sugars after inversion. . . .	0.57	0.56	0.57	0.66	0.41
Sucrose. . . . .	0.50	0.40	0.39	0.58	0.33
Total acid as acetic . . . . .	0.47	0.46	0.47	0.44	0.41
Volatile acid as acetic . . . . .	0.34	0.32	0.20	0.18	0.27
Oil. . . . .	84.84	85.91	86.06	82.51	86.22
Cottonseed oil . . . . .	8.26	Present	Present	Present	Present
Peanut oil . . . . .	16.52	Present	Present	Present	Present
Lecithin-phosphoric acid . . . . .	0.055	0.054	0.058	0.058	0.069
Equivalent to whole eggs . . . . .	19.0	19.28	20.72	20.72	24.64
Equivalent to whole egg solids. . . .	5.0	5.58	5.46	5.46	6.49
Equivalent to egg yolks . . . . .	0.4	6.33	7.05	7.05	8.39
Equivalent to egg yolk solids. . . .	3.2	3.20	3.44	3.44	4.09

#### COMMENTS BY COLLABORATORS.

The following comments and suggestions were made by collaborators:

*John H. Bornmann.*—No difficulty was experienced in the manipulation required in the analysis by these methods other than might be expected with a product of this consistency. It is believed that the methods used will give a very close estimate of the composition of the dressing.

*Raymond Hertwig.*—No important difficulties were encountered in the analysis. In the determination of total solids the samples were dried in a water oven for about two hours before being placed in the vacuum oven.

*W. S. Hubbard.*—It was difficult to get good samples of this dressing owing to the fact that the egg coagulated and separated. There should be room for improvement in total solids determination. The heating in the water oven coagulates the egg, making drying to constant weight a long-drawn-out affair. The oil extracted by alcohol caused bumping in the lecithin-phosphoric acid.

## DISCUSSION OF RESULTS AND COMMENTS.

It is believed that the results are as satisfactory as might be expected from a mixture of this type. It will be noted that the results obtained by Hubbard vary somewhat from those reported by the other collaborators. However, it may be inferred from his remarks that his sample was badly separated at the time of analysis, and undoubtedly this condition rather than faulty manipulation or methods is responsible for his results.

The results submitted and other observations show that the methods used are quite satisfactory. It would seem, however, from the small number of collaborators who have participated in this work and from the unsatisfactory condition of the samples in one instance, that the methods might well be tried out another year on samples containing a smaller percentage of oil and some binding material, in order that undue separation of oil will not occur before analysis is undertaken.

It would also seem, since no general procedure for the determination of lecithin-phosphoric acid is now included in the official and tentative methods and since certain modifications of the details given in the methods have been proposed from time to time, that it would be desirable to investigate these in connection with this study.

## RECOMMENDATIONS.

It is recommended—

(1) That the methods given be resubmitted to collaborators. The samples submitted should contain a smaller proportion of oil and a binder, and should be in the form of a stable, uniform emulsion.

(2) That in addition to the method for lecithin-phosphoric acid as submitted this year, there be studied, also, any available modifications thereof.

## CRUDE FIBER IN PREPARED MUSTARD.

Last year details were submitted for the determination of crude fiber in prepared mustard. Since, however, a change was made in the official general method for crude fiber, the details submitted for prepared mustard were referred back to the Associate Referee on Spices, for study in connection with the changed general method.

Through an unfortunate misunderstanding the associate referee was under the impression that this subject was to be considered by the Associate Referee on Crude Fiber, rather than by himself. It was late in the season when the misunderstanding was cleared up, and as a result no actual collaborative work was done.

The details submitted last year contemplate merely the preliminary steps which are necessary in order to prepare the material for the actual crude fiber determination, and do not contemplate any change whatever

in the method itself. Therefore, any change in the general crude fiber method would automatically also change the method for mustard. (In last year's recommendation the details were given for the entire process merely for the sake of convenience.) In view of the satisfactory results reported last year, it is believed that the preliminary details as described should now be adopted.

#### RECOMMENDATION.

It is recommended that the following details for the determination of crude fiber in prepared mustard be adopted tentatively:

Weigh 10 grams of the sample and transfer to an 8 ounce nursing bottle with 50 cc. of strong alcohol, stopper, and shake vigorously. Add 40 cc. of ethyl ether, shake, and let stand about 5 minutes with occasional shaking. Centrifuge and decant off the alcohol-ether mixture. Treat twice more with 40 cc. portions of ether, shaking, centrifuging, and decanting as before. Rest the bottle on its side for a short time, without heat, to allow the ether largely to evaporate. Transfer the material to a 1000 cc. Erlenmeyer flask using 200 cc. of boiling-hot dilute sulfuric acid and proceed as directed in VII, 66<sup>1</sup>.

If preferred, the sample may be treated with the alcohol and ether in a small beaker, then transferred to a hardened 11 cm. filter paper and washed several times with ether, and finally transferred to a 1000 cc. Erlenmeyer flask with 200 cc. of boiling-hot dilute sulfuric acid.

### REPORT ON THE DETERMINATION OF CACAO SHELLS IN CACAO PRODUCTS.

By V. A. PEASE (Bureau of Chemistry, Washington,  
D. C.), *Referee*.

At the last meeting of the association a method for the determination of cacao shells in cacao products was presented and tentatively adopted<sup>2</sup>. This method provides for the micro-analysis of samples of cacao products and sweetened cacao products, and gives directions for the preparation of such samples for micro-analysis by a simple process of defatting, or defatting and desugaring.

The method is based on the fact that embedded in the shell of the cacao bean there is a single layer of stone cells whose structure is highly characteristic. In the process of grinding the nibs, the fragments of shell that are not fanned out in the cleaning process or that may be deliberately added to the cleaned nibs are still further broken up, and when the material is suitably prepared can be recognized under the microscope with comparative ease. These fragments of stone-cell tissue are counted, and the counts are compared with those obtained on standard preparations of known shell content.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 98.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 99.

In using the method in the analysis of commercial samples, the question has been raised as to whether the water and alcohol used as solvents for the sugar in a sweet chocolate product would appreciably affect the determination of shell content. In order to ascertain the extent to which the results might be affected, the referee washed portions of a 2 per cent standard and a 4 per cent standard with water and alcohol, as directed for desugaring a commercial sample. The bottles were then labelled by a coworker and the preparations counted as unknowns. From the results obtained both by the referee and by the writer, it was evident that while the counts on the washed preparations averaged a trifle higher than those on the unwashed standards, the difference in counts fell within the limits of error of the method and was not sufficient to influence appreciably the final report on a sample.

It was also suggested that it might be advisable, because of a possible saving in time and labor, to leave the sugar in the sample, weigh out a 5 milligram portion of the defatted material for counting, and calculate to a basis of 2 milligrams of fat- and sugar-free material. In accordance with this suggestion four samples were prepared. Both the 2 per cent and the 4 per cent standards were made up with 60 per cent and with 80 per cent of sugar, these representing approximately the minimum and maximum percentages of sugar found in commercial samples, calculated on the fat-free basis. In this instance, 5 milligrams of the preparation containing 60 per cent of sugar were equivalent to 2 milligrams of its corresponding sugar-free standard, while 5 milligrams of the preparation containing 80 per cent of sugar were equivalent to 1 milligram of its corresponding sugar-free standard. It was thus easy to compare results. The four preparations—2 per cent standard+60 per cent sugar, 2 per cent standard+80 per cent sugar, 4 per cent standard+60 per cent sugar, and 4 per cent standard+80 per cent sugar—were labelled by a co-worker, counted as unknowns both by the referee and by the writer, and the results were compared with counts on the original standards. The counts do not appear to have been affected by the presence of the sugar, and the time and labor involved in preparation of the sample for counting are materially lessened. Hence, it seems that this change in the method of preparation of the sample for micro-analysis is at least worthy of further study.

The recent great increase in the use of cacao products to which milk has been added has made desirable a study of the preparation of samples of such products for micro-analysis, since the method tentatively adopted does not cover this phase of the problem as fully as seems warranted at the present time.

The Microchemical Laboratory, working with the Food Control Laboratory, reached the conclusion that probably the safest procedure to follow would be

(1) To obtain chemical data for the fat, sugar, and milk-solid content from a portion of the sample,

(2) To make microscopical counts on 5 milligram mounts of another portion of the sample which had been defatted only, and

(3) To calculate the shell count obtained to a basis of 2 milligrams of the fat-, sugar-, and milk-free cacao material.

Work along this line had just begun when the referee, B. H. Silberberg, resigned her position with the Bureau of Chemistry, and the micro-analytical work on cacao products was assigned to the present referee.

About this time the New York Station suggested an elaborate plan for defatting and desugaring sweet chocolate and milk chocolate products by means of repeated centrifugings with ether, warm water, warm alcohol, and finally with ether. The method involved also the use of factors for sugar and milk content, its author claiming that such a method materially shortened the time for analyzing a sample over that required by a detailed chemical analysis.

It occurred to the referee that in such a method of preparation the loss of material by manipulation might constitute a grave source of error. It would seem, also, that the less preliminary handling a sample receives, the more nearly would the cacao material remain in its original condition, and the greater would be the accuracy in the count.

Another suggestion for desugaring a sweetened cacao product, made by the Seattle Station, was that 70 per cent alcohol be used as a solvent instead of water, as all the sugar would be removed, while the insoluble material would settle completely when centrifuged, thus making it very easy to decant the solution and assuring more accurate results. This would seem to overcome the difficulty mentioned in the discussion of the New York method—the loss of material by manipulation.

In view of the fact that four methods for preparing sweet chocolate and milk chocolate products for micro-analysis were thus before the referee, it was decided to try them out under the same conditions and to compare the results. After conference with the Food Control Laboratory, samples were selected, and a chemist was detailed to prepare the material for microscopic work.

The samples chosen were from an investigational series already on hand, and consisted of a sweet chocolate coating, a milk chocolate coating of low milk content, and a milk chocolate coating of high milk content, each from a different manufacturer.

The methods used were—

(1) The method<sup>1</sup> tentatively adopted by the association, which reads as follows:

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 99.

Eliminate the fat with gasoline or ether in a centrifuge or on a suction filter. In the case of chocolate, shave the sample off so that the defatting agent will penetrate easily. Wash the sample three or four times. If necessary, remove the sample to a mortar, grind, and then continue the defatting process to completion. If the sample contains sugar, remove by washing several times with water in the same way, and wash finally with a mixture of ether and alcohol. Dry, powder, and mix the sample thoroughly, weigh accurately 2 mgs. and mount on a glass slide \* \* \* \*. Examine the entire mount, counting all the stone-cell groups present.

(2) The method suggested by the New York Station:

A charge of approximately 30 grams in the case of sweet chocolate or milk chocolate, and 15 grams in the case of chocolate liquor or cocoa is defatted three times in a centrifuge bottle with 100 cc. portions of ordinary ethyl ether. The bottles are placed on a water bath to expel traces of ether. In the case of the sweet preparations, the residue is washed five times with 100 cc. portions of warm water, approximately 50°C., then

*Comparative data obtained by*

TYPES OF PRODUCT	(1) A. O. A. C. METHOD			
	Bottle A		Bottle B	
	Count 1	Count 2	Count 1	Count 2
<b>A. Sweet chocolate</b>				
Average of counts on two slides .....	155	.....	.....	.....
Computed count .....	—	.....	.....	.....
Per cent shell .....	12.0	.....	.....	.....
Per cent shell, average of all counts .....	—	.....	.....	.....
Weight of residue (grams) .....	6.10	.....	.....	.....
Per cent residue from chemical data .....	16.34	.....	.....	.....
Per cent residue from weight of original sample .....	20.3	.....	.....	.....
Per cent loss by manipulation .....	—	.....	.....	.....
Per cent not removed by manipulation ..	3.96	.....	.....	.....
<b>B. Milk chocolate with low milk content</b>				
Average of counts on two slides .....	111	.....	99.5	.....
Computed count .....	—	.....	—	.....
Per cent shell .....	8.5	.....	7.6	.....
Per cent shell, average of all counts .....	—	.....	8.0	.....
Weight of residue (grams) .....	1.86	.....	1.86	.....
Per cent residue from chemical data .....	8.70	.....	8.70	.....
Per cent residue from weight of original sample .....	6.2	.....	6.2	.....
Per cent loss by manipulation .....	2.5	.....	2.5	.....
Per cent not removed by manipulation ..	—	.....	—	.....
<b>C. Milk chocolate with high milk content</b>				
Average of counts on two slides .....	33.5	37.5	33	30.5
Computed count .....	—	—	—	—
Per cent shell .....	2.5	2.8	2.5	2.3
Per cent shell, average of all counts .....	—	—	—	2.6
Weight of residue (grams) .....	2.74	.....	2.36	—
Per cent residue from chemical data .....	9.57	—	9.57	—
Per cent residue from weight of original sample .....	9.13	.....	7.86	.....
Per cent loss by manipulation* .....	0.44	.....	1.71	.....
Per cent not removed by manipulation ..	—	.....	—	.....

\*Does not account for insoluble milk residue; hence loss of cacao material is greater.

three times with warm alcohol (100 cc., 50 cc. and 50 cc.), and finally with two washings of 50 cc. of ether. The material is placed in a water oven to dry, then put twice through a 100 mesh sieve to mix thoroughly. The preparation of the slide from this dry mixed material is the same as in the tentative official method. In the case of sweet chocolate, 80% of the results is taken as a correct shell count. In the case of milk chocolate, since the average material washed out is about 30%, 70% of the total shell count is taken as the correct value.

### (3) The method suggested by the Seattle Station:

A portion of the sample was extracted once with petroleum ether in the usual manner for preparation of chocolate products for microscopical examination. It was then extracted twice more with ethyl ether, then three times with 70% alcohol, once with 95% alcohol, and once more with ethyl ether. The product was then dried and ground to pass through a 100 mesh sieve, in the usual manner.

*four different methods.*

(2) NEW YORK STATION METHOD				(3) SEATTLE STATION METHOD			(4) MICROCHEMICAL METHOD		
Bottle C		Bottle D		Bottle E			Count 1	Count 2	Chemical Analysis
Count 1	Count 2	Count 1	Count 2	Count 1	Count 2	Count 3			
239.5	.....	243.5	.....	182.5	.....	.....	139.5	.....	Sucrose..... <i>per cent</i> 49.32
199.2	.....	202.9	.....	—	.....	.....	225	.....	Total fat . . . 34.34
15.3	.....	15.6	.....	14.0	.....	.....	17.3	.....	83.66
—	.....	15.4+	.....	—	.....	.....	—	.....	Fat- and sugar-free
4.13	.....	4.21	.....	5.33	.....	.....	.....	.....	cacao material by
16.34	.....	16.34	.....	16.34	.....	.....	.....	.....	difference .16.34
13.76	.....	14.03	.....	17.76	.....	.....	.....	.....	
2.58	.....	2.31	.....	—	.....	.....	.....	.....	
—	.....	—	.....	1.42	.....	.....	.....	.....	
102	.....	.....	.....	71	.....	.....	36	.....	Sucrose..... 34.81
78.4	.....	.....	.....	—	.....	.....	90	.....	Milk solids less milk
6.0	.....	.....	.....	5.4	.....	.....	7.0	.....	fat . . . 8.91
—	.....	.....	.....	—	.....	.....	—	.....	Total fat . . . 47.58
1.77	.....	.....	.....	2.75	.....	.....	.....	.....	91.30
8.70	.....	.....	.....	8.70	.....	.....	.....	.....	Fat-, sugar- and
5.90	.....	.....	.....	9.16	.....	.....	.....	.....	milk-free cacao
2.8	.....	.....	.....	—	.....	.....	.....	.....	material by differ-
—	.....	.....	.....	0.42	.....	.....	.....	.....	ence . . . 8.70
54	50	30.5	31	42	25	30	14	11	Sucrose..... 40.35
41.5	38.6	23.4	23.8	—	—	—	37.3	28	Milk solids less milk
3.2	2.9+	1.8	1.8	3.2	1.9	2.3	2.8	2.1	fat . . . 13.35
—	—	—	2.4	—	—	2.5	—	2.6	Total fat . . . 36.73
2.46	.....	2.61	—	3.83	.....	—	.....	—	90.43
9.57	.....	9.57	.....	9.57	.....	.....	.....	.....	Fat-, sugar-, and
8.20	.....	8.66	.....	12.76	.....	.....	.....	.....	milk-free cacao
1.93	.....	0.91	.....	—	.....	.....	.....	.....	material by differ-
—	.....	—	.....	3.19	.....	.....	.....	.....	ence . . . 9.57



(4) The method worked out by the Microchemical Laboratory in collaboration with the Food Control Laboratory:

Defat the material, dry, powder, and thoroughly mix, as prescribed by the tentative official method. Weigh 5 mgs. of the material so prepared, instead of 2 mgs., as officially prescribed; mount; and count as usual. Make a chemical analysis of another portion of the sample to determine the amount of fat and sugar, or fat, sugar, and milk solids present, and compute the count on 5 mgs. of fat-free material to the basis of 2 mgs. of fat- and sugar-free, or fat-, sugar-, and milk-free material.

In the first three methods of preparation, 30 gram samples were run. In the fourth method, results already obtained and officially reported were used. The results obtained by the four methods have been tabulated for ease in comparison. Time does not permit a detailed discussion of the figures submitted, but it may be noted that while there is a small variation in the results obtained by the different methods, a similar variation is found in some cases between duplicate bottles by the same method. It is also noteworthy that an average of all counts under each method brings surprisingly concordant results. While the percentage of loss by manipulation appears to be fairly large in some cases, and to vary quite noticeably in the different methods, and even between duplicate bottles by the same method, this variation, when reduced to terms of a 2 milligram mount, becomes practically negligible. The method itself is not accurate to such a degree that the results would be noticeably affected by so small a difference.

The use of 5 milligrams of a fat-free mixed chocolate product appears at first thought to effect an increase in the amount of cacao material on the slide, and thus to make counting more difficult. However, in 15 samples of milk chocolate products examined by the referee in the last few months, the actual amount of fat-, sugar-, and milk-free cacao material on the slide in a 5 milligram mount averaged 0.76 milligram and in only one case did the cacao material run over 1 milligram. The milk and sugar present in the mount act as diluents (this is highly desirable in a sample running high in shell content); both are dissolved in the mounting medium, so that accuracy in counting is not interfered with; and an increased accuracy in weighing is attained.

The summary of the results accomplished by the Referees on the Determination of Cacao Shell in Cacao Products shows that at the present time sufficient progress has not been made to justify making any recommendations. The work has, however, reached a point from which a plan for another year can be clearly outlined, and it is suggested that during the coming year as much time as possible be devoted to careful work along the lines already started—a method for the preparation for microscopic examination of sweet chocolate and milk chocolate products to supplement the method already tentatively adopted by this association.

## RECENT ANALYSES OF CACAO BEANS AND THEIR SIGNIFICANCE.

By W. C. TABER (U. S. Food and Drug Inspection Station, Philadelphia, Pa.<sup>1</sup>) and M. L. OFFUTT (Bureau of Chemistry, Washington, D. C.<sup>2</sup>).

The senior author, two years ago at the meeting of this association, presented a report on "The Determination of Shells in Cacao Products"<sup>3</sup>, in which the methods for determining the amount of shells were briefly reviewed. The conclusion was that the crude fiber is the most important single determination that can be made. Since this determination is so important, even though it does not show small amounts of shells in cacao products, it was thought advisable to obtain further data on authentic samples of different varieties of beans free from shell as well as data on the shell itself. Twelve analyses of seven varieties of beans were given in the previous report. Thirty samples have since been examined, representing twelve varieties of roasted beans, many of them being in common use at the present time. The results obtained are shown in Table 1.

Some interesting facts are shown in Table 1. The fat content of these beans is seen to be well above 50 per cent, the average being nearly 54 per cent. The high ash is particularly noticeable in two samples, Arriba and Maracaibo, but in only one of these is the acid-insoluble ash high. In two other samples of Arriba beans not quoted in the table, the total ash was found to be over 8 per cent. The high acid-insoluble ash is also noted in one sample of Trinidad beans, while one other sample of Trinidad is normal in this respect. This same variation has been observed in other samples not reported in this table, and its significance is not apparent.

The ratio of the crude fiber to total ash has been given as an indication of the use of shell or "fines", as the small particles of finely divided cocoa material, largely shell, are technically known. In case of added shell or "fines" the ratio of crude fiber to total ash has been given as exceeding one to one. It will be observed, however, that in half of these authentic samples the crude fiber exceeds the total ash, and notably in all the Accra and Bahia beans.

The crude fiber figure is worthy of note, as 11 samples are over 7 per cent, although the average of the 30 samples is only slightly above that figure. The tendency to high fiber is observed in the Accra, Bahia, Trinidad, and Maracaibo beans, in most of which high ash was also

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<sup>3</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 253.

found. It might be added that some of these are also high-grade beans. The high fiber content was first noted in the Accra variety, grown on the West coast of Africa, and now composing a large proportion of the beans of commerce, having come into common use during the last few years. Owing to its extensive use, it was thought best to analyze a number of samples of this variety. It may be noted that most of them come under 7 per cent in crude fiber, although the average of the seven samples would be higher. In the case of Trinidad and Bahia beans there seems to be a more uniform tendency to a high figure for this determination, although it would seem probable, judging from the analyses of other beans, that if a large number of samples had been analyzed many would have been found below 7 per cent in crude fiber.

TABLE 1.  
*Results of analyses of authentic samples of cacao beans free from shell.*

VARIETY	FAT	ASH*			CRUDE FIBER*
		Total	Water-Insoluble	Acid-Insoluble	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Accra.....	54.98	6.53	3.69	0.05	6.83
Accra.....	52.38	5.58	2.93	0.00	9.21
Accra.....	51.28	6.43	2.65	0.10	6.53
Accra.....	51.08	8.15	4.36	0.43	9.70
Accra.....	52.75	6.55	3.38	0.04	6.78
Accra.....	55.23	5.81	3.38	0.00	6.59
Accra.....	55.02	6.34	3.09	0.00	6.36
Arriba.....	55.29	8.39	4.76	0.05	5.89
Arriba.....	55.43	8.84	4.74	0.07	5.87
Arriba.....	55.96	11.59	4.42	0.70	6.79
Bahia.....	52.58	6.27	3.47	0.00	6.93
Bahia.....	56.45	6.66	3.89	0.12	7.78
Bahia.....	57.39	6.04	3.24	0.00	7.71
Bahia.....	53.92	7.37	3.29	0.09	7.62
Caracas.....	54.65	7.88	4.00	0.04	6.97
Caracas.....	52.05	8.22	4.33	0.00	6.93
Caracas.....	52.01	7.61	4.28	0.25	6.02
Maracaibo.....	53.48	8.00	3.67	0.00	7.52
Maracaibo.....	52.31	10.68	3.84	0.00	9.83
Porto Cabello.....	53.23	7.57	3.87	0.11	6.39
Sanchez.....	53.19	8.01	4.27	0.00	6.14
Costa Rican.....	55.94	5.39	3.75	0.05	8.42
Ceylon.....	54.58	9.10	4.67	0.00	6.55
Guyaquil.....	55.65	8.18	4.74	0.00	6.52
Para.....	54.43	6.85	4.18	0.07	7.65
Trinidad.....	54.02	7.07	3.52	0.07	7.14
Trinidad.....	50.93	7.58	3.62	0.06	7.98
Trinidad.....	52.04	6.84	3.47	0.04	6.82
Trinidad.....	51.63	7.87	3.95	1.27	7.96
Arriba, Bahia and Trinidad.....	53.19	7.56	3.72	1.11	7.01
Average.....	53.77	7.50	3.84	0.157	7.21
Maximum.....	57.39	11.59	4.76	1.27	9.83
Minimum.....	50.93	5.39	2.65	0.00	5.87

\*Calculated on moisture-fat-free basis.

This variation in the same variety of bean might be expected under the varying conditions of culture and growth. It may be seen that the average of all these samples is 7.21 per cent. If the 12 samples reported in 1920 had been included in this tabulation the average for the 42 samples would have been 7.02 per cent.

In the estimation of the amount of shell in cacao products by the crude fiber method it is essential to know what the fiber figure is for authentic samples of shells as well as that for the cleaned beans or nibs. The results shown in Table 2 were obtained on 18 samples of shell taken from seven varieties of beans.

TABLE 2.  
*Results of determination of cacao shell.*

VARIETY	FAT	ASH*			CRUDE FIBER*
		Total	Water-Insoluble	Acid-Insoluble	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Accra.....	5.88	9.77	4.32	1.49	23.47
Arriba.....	6.43	9.73	3.27	1.09	14.85
Bahia.....	5.78	9.24	3.73	0.38	19.47
Caracas.....	5.28	23.90	19.41	8.34	12.68
Sanchez.....	6.45	10.14	4.97	0.92	21.28
Trinidad.....	4.93	29.38	25.59	14.91	15.52
Average.....	5.79	15.36	10.21	4.52	17.88
Maximum.....	6.45	29.38	25.59	14.91	23.47
Minimum.....	4.93	9.24	3.27	0.38	14.85

\*Calculated on moisture-fat-free basis.

With regard to the data in Table 2, the high ash observed in two samples is accounted for largely by the claying of the beans, and partly by the drying on the shell of the pulpy matter surrounding the bean during the fermentation process. The figures, disregarding the variation due to these causes, are quite constant, and referring to these and other analyses made by the authors it has normally been found to be about eight to ten per cent. The average fiber figure is nearly 18 per cent, which corresponds closely to the average figure of 18.7 given in 1920 on 12 samples of shell. The average of all samples examined would be 18.5 per cent.

It might be worth while to refer to Table 1 in the 1920 report<sup>1</sup> in which crude fiber results are given on roasted beans or nibs and roasted shell as obtained by various workers in this country and in England. The work reported in this paper would slightly modify the figures there given, which, as indicated previously, would extend the limits for fiber on the bean and raise the average figure from 6.5 to 7.0 per cent. This

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 254.

tendency to raise this figure is doubtless accounted for by the marked change in the varieties of beans being used at the present time. The change in the limits for the fiber in the roasted shell is seen, however, to be very small, and the average (17.9) is only a little lower than that reported previously. The average of all samples of shell as given in Table 2 and of those reported previously would only lower this figure from 18.7 to 18.5 per cent.

In view of the importance of the crude fiber determination in estimating the amount of shell present in cacao products, it seems advisable that the empirical method be standardized as closely as possible, as advised by G. L. Bidwell and others, particularly as there seems to have been considerable variation in the procedure as followed by different analysts of cacao products.

## REPORT ON METHODS FOR EXAMINATION OF CACAO BUTTER.

By WALTER F. BAUGHMAN (Bureau of Chemistry, Washington, D. C.),  
*Referee.*

This report is concerned with two qualitative tests for detecting foreign fat in cacao butter. The first test, which is similar to the Valenta test<sup>1</sup>, consists in comparing the critical temperature of dissolution in acetic acid of the sample under examination with that of cacao butter. Practically each of the potential substitutes for cacao butter, with the notable exceptions of tallow, hydrogenated oils, and paraffin, has a critical temperature of dissolution below that of cacao butter, and the dissolution temperatures of mixtures of cacao butter and these substitutes are lower than the dissolution temperature of cacao butter by amounts approximately proportional to the amounts of substitute present. This test is designed to detect coconut, palm kernel, cottonseed oils or stearines, corn oil, peanut oil, etc., but not tallow, hydrogenated oils, or paraffin.

The second test, which was first proposed by Eugene Bloomberg, is designed to detect tallow, hydrogenated oil, and paraffin, but not the other possible substitutes mentioned previously. It is based on the greater insolubility of tallow, hydrogenated oils, and paraffin in a mixture of equal parts of acetone and carbon tetrachloride.

These two methods were submitted to collaborators by Bloomberg, the referee in 1916. The collaborative results were quite satisfactory, but the Committee on Recommendations of Referees thought that

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<sup>1</sup> *J. Soc. Chem. Ind.*, 1884, 3: 643.

these methods should be studied further<sup>1</sup>. At the 1920 meeting of the association, the present referee read a report on a critical examination of these two methods<sup>2</sup>. This examination showed, in regard to the first test, that the acidity of the fat influences the critical temperature of dissolution; that the variation is proportional to the amount of acidity; and that it is possible to correct the results by the use of a proper factor. The constancy of the critical temperature of dissolution of cacao butter produced under different conditions of manufacture and from beans grown in different localities was proved by the examination of a number of pure samples. In 1921, these two methods were submitted to collaborators, but for various reasons reports were received from three only. The results obtained with the critical temperature of dissolution test by one collaborator were very satisfactory, but those reported by the other two were not satisfactory. All three obtained good results with the acetone-carbon tetrachloride test.

#### COLLABORATIVE WORK.

The methods with directions, as published by Committee C on Recommendations of Referees<sup>3</sup>, were sent to the collaborators.

The following samples were sent to the collaborators:

1. A mixture of cacao butter and 20% peanut oil.
2. A mixture of cacao butter and 5% hydrogenated cottonseed oil.
3. A mixture of cacao butter and 10% coconut oil stearine.
4. A mixture of cacao butter and 10% tallow.
5. A mixture of cacao butter and 15% cottonseed oil stearine.
6. A mixture of cacao butter and 10% palm kernel oil stearine.
7. Pure cacao butter with a rather high acidity.

A sample of pure cacao butter to be used as a standard was also sent.

#### DISCUSSION.

All the analysts agree that the critical temperature of dissolution showed samples Nos. 1, 3, 5, and 6 to be adulterated. These samples contained, respectively, 20 per cent peanut oil, 10 per cent coconut oil stearine, 15 per cent cottonseed oil stearine, and 10 per cent palm kernel oil stearine. All except one reported no indication of foreign fat in sample No. 2 and all except two, no indication in sample No. 4. These two samples contained, respectively, hydrogenated cottonseed oil and tallow and should have given negative results. For sample No. 7, which was pure cacao butter with a rather high acidity, five of the analysts reported no adulteration; one, a "slight indication" of adul-

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1920, 3: 486.

<sup>2</sup> *Ibid.*, 1921, 5: 263.

<sup>3</sup> *Ibid.*, 1923, 6: 278.

*Results of collaborative work on cacao butter samples.*

ANALYST*	ACID VALUE	CRITICAL TEMPERATURE OF DISSOLUTION				CONCLUSION AS TO PURITY	ACTONE-TETRACHLORIDE TEST
		Found °C.	Corrected °C.	Variation from Pure Cacao Butter			
Pure cacao butter used as standard.							
1	1.33	98.0	99.6	.....	.....	.....	
2	1.40	96.5	98.2	.....	.....	.....	
3	1.41	84.0	85.7	.....	.....	.....	
4	1.40	98.7	100.4	.....	.....	.....	
5	1.25	94.0	95.5	.....	.....	.....	
6	1.40	90.9	92.6	.....	.....	.....	
7	1.12	96.0	97.3	.....	.....	.....	
Sample No. 1.							
1	4.82	90.0	95.8	-3.8	Adulterated	Negative	
2	5.04	87.5	93.6	-4.6	Adulterated	Negative	
3	4.78	75.4	81.1	-4.6	Adulterated	Negative	
4	4.90	90.2	96.1	-4.3	Adulterated	Negative	
5	4.87	81.1	86.9	-8.6	Adulterated	Slightly positive	
6	4.81	71.8	77.6	-15.0	Adulterated	Negative	
7	4.37	77.6	82.8	-4.5	Adulterated	Negative	
Sample No. 2.							
1	1.36	98.0	99.6	0.0	Adulteration not shown	Positive	
2	1.45	97.0	98.7	+0.5	Adulteration not shown	Positive	
3	0.66	84.8	85.6	-0.1	Adulteration not shown	Positive	
4	1.45	99.4	101.1	+0.7	Adulteration not shown	Positive	
5	1.36	93.8	95.4	-0.1	Adulteration not shown	Positive	
6	2.44	89.9	92.8	+0.2	Adulteration not shown	Positive	
7	1.46	91.0	92.8	-4.5	Adulterated	Positive	
Sample No. 3.							
1	1.33	89.5	91.1	-8.5	Adulterated	Negative	
2	1.34	87.0	88.6	-9.6	Adulterated	Negative	
3	0.61	81.4	82.1	-3.6	Adulterated	Negative	
4	1.34	90.9	92.5	-7.9	Adulterated	Negative	
5	1.28	84.9	86.4	-9.1	Adulterated	Negative	
6	1.49	75.5	77.3	-15.3	Adulterated	Negative	
7	1.34	66.4	68.0	-29.3	Adulterated	Negative	
Sample No. 4.							
1	1.36	97.0	98.6	-1.0	Adulteration not shown	Positive	
2	1.45	95.0	96.7	-1.5	Adulteration not shown	Positive	
3	1.31	82.6	84.2	-1.5	Adulteration not shown	Negative	
4	1.45	99.2	100.9	+0.5	Adulteration not shown	Positive	
5	1.35	94.0	95.6	+0.1	Adulteration not shown	Positive	
6	1.49	85.0	86.8	-5.8	Adulterated	Positive	
7	1.46	86.0	87.8	-9.5	Adulterated	Negative	

*Results of collaborative work on cacao butter samples—Continued.*

ANALYST*	ACID VALUE	CRITICAL TEMPERATURE OF DISSOLUTION			Conclusion as to Purity	ACETONE-TETRACHLORIDE TEST
		Found °C.	Corrected °C.	Variation from Pure Cacao Butter		

*Sample No. 5.*

1	6.89	86.5	94.8	-3.6	Adulterated	Negative
2	7.23	83.0	91.7	-6.5	Adulterated	Negative
3	6.72	71.4	79.4	-6.3	Adulterated	Negative
4	7.00	89.2	97.6	-2.8	Adulterated	Positive
5	6.86	77.6	85.8	-9.7	Adulterated	Positive
6	8.50	72.8	83.0	-9.6	Adulterated	Negative
7	6.38	86.8	94.5	-2.8	Adulterated	Negative

*Sample No. 6.*

1	4.68	86.0	91.6	-8.0	Adulterated	Negative
2	4.70	82.5	88.2	-10.0	Adulterated	Negative
3	4.52	71.0	76.4	-9.3	Adulterated	Negative
4	4.76	88.1	93.8	-6.6	Adulterated	Negative
5	4.52	81.4	86.8	-8.7	Adulterated	Slightly Positive
6	4.81	74.0	79.8	-12.8	Adulterated	Negative
7	4.14	72.2	77.2	-20.1	Adulterated	Negative

*Sample No. 7.*

1	7.06	91.5	100.0	+0.4	Adulteration not shown	Negative
2	7.28	88.0	96.7	-1.5	Adulteration not shown	Negative
3	6.76	76.4	84.5	-1.2	Adulteration not shown	Negative
4	7.28	95.6	104.3	+4.3	Adulteration not shown	Very slightly positive
5	6.78	84.9	93.0	-1.4	Adulteration not shown	Negative
6	7.37	81.3	90.2	-2.4	Adulterated (slight indication)	Negative
7	6.11	74.4	81.7	-15.6	Adulterated	Negative

## \*Analysts—

1. Walter F. Baughman, Bureau of Chemistry, Washington, D. C.
2. Philip L. Gowen, Bureau of Chemistry, Washington, D. C.
3. W. C. Taber, U. S. Food and Drug Inspection Station, Philadelphia.
4. E. H. Berry, U. S. Food and Drug Inspection Station, Chicago.
5. Edward R. Miller, U. S. Food and Drug Inspection Station, New York.
6. Raymond M. Hann, Bureau of Chemistry, Washington, D. C.
7. Marie L. Offutt, Bureau of Chemistry, Washington, D. C.; present address, U. S. Food and Drug Inspection Station, New York.

teration; and the other found it to be adulterated. The results on the last sample show the necessity for a correction for acidity. If the results had not been corrected for acidity all analysts would, undoubtedly, have reported this sample to be adulterated. Forty-nine critical temperature of dissolution tests were made; forty-four correct and five incorrect results were obtained. Five analysts obtained correct results for all seven samples; one analyst obtained correct results for five samples, and the other correct results for four samples.



All the analysts agree that the acetone-carbon tetrachloride test showed sample No. 2, which contained 5 per cent hydrogenated cotton-seed oil, to be adulterated; while for sample No. 4, which contained 10 per cent tallow, five reported adulteration and two no adulteration. For sample No. 7, pure cacao butter, there are six negative results and one 'slightly positive' result. For the most part negative results were obtained for the other samples. There are forty-two correct results, four incorrect ones, and three that may be classed as doubtful. Three analysts obtained correct results for all seven samples; two obtained correct results on six samples; one analyst reported five correct results, one incorrect one, and one doubtful one; and the other analyst reported four correct results, one incorrect one, and two doubtful ones.

### RECOMMENDATIONS.

It is recommended—

(1) That the critical temperature of dissolution test be adopted as a tentative method.

(2) That the acetone-carbon tetrachloride test be adopted as a tentative method.

No report was made by the Referee on Coffee.

### REPORT ON TEA.

By R. E. ANDREW (Agricultural Experiment Station, New Haven, Conn.), *Referee*.

The work this year has been devoted chiefly to a study of methods for determining the water extract in tea. The present tentative method, originally suggested by Doolittle and Woodruff<sup>1</sup>, derives extractive matter indirectly by determining the percentage of insoluble leaf. The objection to this procedure is that it is time-consuming, owing principally to the slow filtration. Modifications have been suggested from time to time. One modification, an adaptation of a procedure used in this laboratory for the determination of crude fiber, was suggested by a former referee on tea<sup>2</sup>. Although the results obtained were good, and the method possessed points of advantage over the tentative method, it was not entirely satisfactory.

McGill<sup>3</sup> and Allen<sup>4</sup> have described methods which obtain the extrac-

<sup>1</sup> U. S. Dept. Agr. Bur. Chem. Bull., 105, 48.

<sup>2</sup> Conn. Exp. Sta. Bull. 210, 182; *J. Assoc. Official Agr. Chemists*, 1921, 4: 537.

<sup>3</sup> Lab. of the Inland Rev. Dept., Ottawa, Canada, Bull. 359.

<sup>4</sup> Allen's Commercial Organic Analysis, Vol. VI, 623.

tive matter in tea by direct evaporation of the aqueous solution. Since this plan largely avoids long filtration and a separate moisture determination, which in itself is a source of considerable variation, it was thought to be worthy of further investigation. Preliminary trials having given promising results a proposed method was outlined and sent to collaborators.

#### COLLABORATION.

Samples were sent and reports received from the following: H. J. Knapp, Department of Health, Cleveland, Ohio—work done by H. K. Newton, W. D. Pack, and P. Tarver; Loren Burritt, Chemical Laboratory, Treasury Department, Washington, D. C.; S. H. Hall, Massachusetts Department of Health, Division of Food and Drugs, Boston, Mass.; A. Papineau-Couture, Department of Health, Ottawa, Canada; A. M. Henry, State Agricultural Department, Tallahassee, Florida; Llewelyn Jones, Junior Chemist, Bureau of Chemistry, Chicago, Ill.; C. F. Whitney, Laboratory of Hygiene, Burlington, Vermont; Miss E. H. Davis, City Health Department, Baltimore, Md.; S. C. Moulton, District of Columbia Health Department, Washington, D. C.; C. E. Shepard and H. J. Fisher, Agricultural Experiment Station, New Haven, Conn.

#### INSTRUCTIONS TO COLLABORATORS.

Eight samples and the following instructions were sent to each collaborator:

##### MOISTURE.

Dry 2 grams of the ground sample, using weighing tubes, at 100°C. for 10 hours.

##### WATER EXTRACT.

###### *Tentative Method<sup>1</sup>.*

To 2 grams of the original sample in a 500 cc. Erlenmeyer flask add 200 cc. of hot water and boil over a low flame for an hour. The flask should be closed with a rubber stopper through which passes a glass tube 30 inches long for a condenser. The loss from evaporation should be replaced from time to time by the addition of hot water. Filter through a tared filter and wash the residue until the filtrate measures 500 cc., stirring the contents of the filter throughout the process to facilitate the filtering. Dry the filter paper and the residue in the funnel in a steam oven till the excess of water is removed, transfer paper and contents to a tared bottle, and dry to constant weight at 100°C. The sum of the percentages of insoluble leaf and of moisture subtracted from 100 per cent gives the percentage of hot water extract.

###### *Proposed Method.*

To 2 grams of the *ground* sample in a 500 cc. graduated flask add 200 cc. of hot water and boil over a low flame for 1 hour, rotating occasionally. The flask should be closed with a rubber stopper through which passes a glass tube 30 inches long for a condenser.

<sup>1</sup> As described in *Assoc. Official Agr. Chemists, Methods*, 1920, 273, except that a longer condenser is used

TABLE 1.  
Water extract in leas.

ANALYST	18616			18617			18618			18619		
	Moisture	Method		Moisture	Method		Moisture	Method		Moisture	Method	
		Tentative	Proposed		Tentative	Proposed		Tentative	Proposed		Tentative	Proposed
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Shepard	6.03*	.....	.....	4.16*	.....	.....	5.60*	.....	.....	6.95*	.....	.....
	6.00	41.0	40.6	4.09	43.1	41.0	5.52	41.1	37.5	6.52	35.9	34.6
Knapp	5.35	40.7	41.2	3.51	41.4	41.1	5.00	40.1	40.8	6.03	38.0	35.6
		41.2	41.6	.....	42.2	41.4		40.2	39.1		34.5	34.3
			41.7	.....		41.6			40.4			35.2
Burritt	5.40	40.2	41.6	3.20	48.6	39.4	4.75	37.8	40.3	4.92	34.2	34.6
	.....	36.7	39.0	.....	46.4	38.4	.....	35.9	36.6	.....	32.5	32.9
Hall	7.55	.....	40.8	4.75	.....	41.5	6.05	.....	39.9	7.85	.....	35.2
	7.70	.....	40.1	4.55	.....	41.7	6.40	.....	39.5	7.40	.....	35.7
Fisher	8.21†	38.8	41.5	7.42†	40.5	40.8	7.17†	39.9	39.5	8.95†	33.5	34.1
Papineau	6.39	40.8	41.3	4.53	42.2	42.2	5.94	39.9	40.8	7.23	34.8	35.9
Couture	6.47	.....	.....	4.52	.....	.....	5.99	.....	.....	7.29	.....	.....
Henry	6.00	40.8	38.7	4.25	40.4	40.4	5.57	38.9	35.1	6.88	33.6	33.6
		39.7	38.9	.....	40.5	39.8		39.1	34.5		34.0	33.5
Jones	5.53	.....	41.3	3.81	44.0	42.3	5.13	43.1	40.4	6.40	35.3	35.5
	5.50	‡	41.9	3.86	44.5	42.0	5.10	43.4	39.2	6.41	35.7	35.6
			42.3	.....	.....	.....					35.8	35.9
Whitney	6.18	38.0	40.4	4.38	38.2	41.0	5.77	37.0	39.2	7.02	30.4	34.4
	6.30	37.9	40.4	4.33	39.0	41.3	5.72	36.2	38.9	6.79	30.7	34.7
Davis	5.68	§	41.1	3.55	§	42.4	5.25	§	40.3	6.41	§	35.6
	5.66		42.1	3.58		42.5	5.24		40.0	6.39		35.9
Moulton	4.93	45.5	42.3	4.25	45.1	42.7	5.22	43.4	40.8	6.67	39.6	36.0
	5.19	.....	42.2	4.23	.....	42.6	5.59	.....	40.9	6.36	.....	36.4
Andrew	6.14	40.1	40.0	4.49	41.0	39.7	5.81	39.2	37.5	6.97	34.4	34.9
	6.28	40.6	40.0	4.42	41.6	40.0	5.81	41.1	37.1	6.89	34.1	34.5
Maximum	8.21	45.5	42.3	7.42	48.6	42.7	7.17	43.4	40.8	8.95	39.6	36.2
Minimum	4.93	36.7	38.7	3.20	38.2	38.4	4.75	35.9	34.5	4.92	30.4	32.9
Average	6.12	40.1	40.9	4.29	42.4	41.1	5.63	39.8	39.0	6.81	34.5	35.0
	18375			18318			18386			18395		
Hall	6.37	36.9	37.8	5.42	37.9	37.7	6.38	38.3	37.5	5.64	36.5	35.7
Fisher	5.88	35.5	36.7	4.93	37.6	38.3	6.18	36.7	37.9	5.20	35.9	37.0
Andrew	6.50	36.7	36.5	5.50	36.7	37.4	6.43	37.6	37.4	5.83	35.0	35.8
Average	6.25	36.4	37.0	5.28	37.4	37.8	6.33	37.5	37.6	5.55	35.8	36.2

\*Moisture on unground sample.

†Moisture on unground sample; flat bottom dish.

‡Broken in transit.

§Report withheld. See comments of analysts.

Boil very slowly so that no steam escapes from the top of the air condenser. Cool, dilute to volume, mix thoroughly, and filter through a dry filter paper. Take an aliquot of 50 cc. and evaporate to dryness over a steam bath. Place in the oven and heat at 100°C. for one hour, cool, and weigh.

## COMMENTS OF ANALYSTS.

*Llewelyn Jones.*—While I have no special comment to make regarding the methods, my choice is in favor of the proposed method, inasmuch as it is more easily manipulated. It seems strange that the proposed method does not give more uniform results.

*C. F. Whitney.*—The proposed method, which involves a simpler process, seems to me to be preferable, not only on account of less time consumed but also on account of the probability of greater accuracy.

*S. H. Hall.*—My figures would indicate that accuracy of the two methods is about the same. The proposed method, however, is much quicker and more convenient.

*W. D. Pack.*—We have no criticisms to make of the proposed method. Any difference in results must be due to the boiling operation as it was found possible to check solids on different 50 cc. portions to within 0.2 milligram. Neither does the time of drying alter results; increasing the time from one hour to two hours gave results much closer than the experimental error in pipetting. In the proposed method Traver substituted a tall-form lipless beaker for the Erlenmeyer flask and used a distilling flask as a water condenser in place of the 30 inch glass tube.

*A. M. Henry.*—I believe that the proposed method is more accurate and will give better results.

*A. Papineau-Couture.*—From the point of view of speed and ease of manipulation the proposed method is, in my mind, far ahead of the tentative method, as it eliminated the moisture determination, the tedious washing of filter paper which is necessarily time-consuming.

*E. H. Davis.*—I am submitting no results on the tentative method for water extract because I could get no constant weights.

*H. J. Fisher.*—The proposed method is, of course, much quicker. It also has the advantage that, as it uses the powdered tea, there is less question as to whether a representative sample was used.

*C. E. Shepard.*—The tentative method for hot water extract in tea has several objectionable features. It is somewhat difficult to transfer all the particles of tea from the flask to the filter paper. The filtration with many samples is very slow, sometimes taking several hours, with the chance of chemical changes taking place owing to fermentation. Uneven sampling is likely to occur using the unground tea. Any error in the moisture determination would cause the same error in the determination of the hot water extract. The manipulation is easy in the proposed method and the objectionable features of the tentative method are eliminated.

#### DISCUSSION.

The averages of all results by the two methods check very well. The differences are well within the limits of experimental error for a determination of this kind, that is, 1 per cent. The best individual checks were obtained by the proposed method.

A number of market teas have been examined by the referee this year, and the water extracts are shown in Table. 2

#### CAFFEINE.

A. Papineau-Couture and H. J. Fisher have submitted results on caffeine in which the Power-Chesnut and the Bailey-Andrew methods were used. The figures by both methods are in good agreement and corroborate the experience of collaborators reported last year.

TABLE 2.

*Results of determinations of water extract in teas obtained by the referee.*

STATION NO.	TENTATIVE METHOD	PROPOSED METHOD
15709	37.5	35.8
15711	35.3	36.7
18312	38.1	38.5
18317	37.5	36.1
18318	36.7	37.4
18320	40.7	41.0
18322	37.9	37.7
18332	38.9	39.5
18339	39.1	38.5
18356	41.6	39.4
18359	35.8	35.5
18367	40.7	39.8
18369	38.4	38.2
18375	36.4	36.5
18376	37.6	37.4
18388	37.8	38.5
18395	35.0	35.8
18397	34.5	33.7
18409	38.6	39.0
Average . . . . .	37.8	37.6

## RECOMMENDATIONS.

It is recommended—

- (1) That the Bailey-Andrew method be adopted as an official method for determining caffeine in tea.
- (2) That the proposed method be adopted as an official method for determining the water extract in tea.
- (3) That suggestions for further study on the subject of tea be left to the next referee.

No report was made by the Referee on Nitrogen in Foods, and it was recommended that this subject be discontinued.

The convention adjourned at 3 o'clock, Friday, November 17. The proceedings for Friday morning and afternoon were published in Volume VI, No. 3.

## CONTRIBUTED PAPERS.

### COMPARISON OF THE ROESE-GOTTLIEB AND BABCOCK METHODS OF TESTING.

#### I.—INDIVIDUAL SAMPLES.

#### II.—FACTORY CONTROL.

By A. O. DAHLBERG (Research Laboratories, California Central Creameries, San Francisco, Calif.).

The object of the investigation was to compare the Roese-Gottlieb<sup>1</sup> and Babcock<sup>1</sup> methods of testing and to determine the cause of continued unaccounted butterfat losses occurring at whole milk creameries operated by the company.

#### OUTLINE OF INVESTIGATION.

The time required for making tests with the official Roese-Gottlieb method made advisable the use of some modification of this method, whereby results could be secured in less time.

To determine the accuracy of the modified Roese-Gottlieb method used, comparative tests with the official Roese-Gottlieb method were made on milk, cream, butter, skimmilk, and buttermilk samples.

Tables 1 and 2, giving the results of the comparison, show the modified Roese-Gottlieb tests, made according to the method used, to check closely with those of the official Roese-Gottlieb method. The modified method used is accurate and gives results corresponding with those secured with the official Roese-Gottlieb method.

#### METHODS USED IN TESTING.

##### *Official Roese-Gottlieb Method.*

The official Roese-Gottlieb methods were used for the determination of butterfat in milk, cream, and butter (direct method).

With buttermilk, skimmilk, and wash water, samples of ten grams each were used, and the test was carried out the same as for milk.

The use of thin Erlenmeyer flasks of 150 cc. capacity eliminated the difficulty experienced at the start—the creeping of the fat solution over the edge of the smaller flasks recommended.

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<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 227.

TABLE 1.  
Comparison of official Roese-Gottlieb and modified Roese-Gottlieb tests on milk,  
cream, and butter.

SAMPLE	AVERAGE OF DUPLICATE TESTS		VARIATION BETWEEN DUPLICATES	
	Roese-Gottlieb (Official)	Roese-Gottlieb (Modified)	Roese-Gottlieb (Official)	Roese-Gottlieb (Modified)
<b>Milk</b>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A2-25 .....	4.53	4.54	0.01	0.01
A2-26 .....	4.41	4.45	0.01	0.01
A2-27 .....	4.54	4.55	No duplicate	0.01
A2-28 .....	4.52	4.53	0.03	0.01
A2-14 .....	4.81	4.82	0.08	0.06
A2-15 .....	4.75	4.75	0.04	0.01
Average .....	4.59	4.61	0.03	0.02
<b>Cream</b>				
A2-25 .....	37.08	37.11	0.07	0.02
E2-25 .....	36.36	36.34	0.04	0.01
E2-26 .....	37.67	37.71	0.11	0.10
E2-27 .....	37.41	37.49	0.02	0.10
SS1 .....	20.14	20.12	0.08	0.03
SS2 .....	30.49	30.51	0.02	0.04
Average .....	33.19	33.21	0.056	0.050
<b>Butter</b>				
E2-16 .....	79.00	79.11	0.09	0.00
E2-25 .....	79.79	79.62	0.06	0.01
E2-26 .....	79.93	79.74	0.02	0.04
E2-28 .....	79.65	79.71	0.04	0.00
S2-17S .....	83.19	83.15	0.09	0.03
Average .....	80.31	80.27	0.05	0.01

TABLE 2.  
Comparison of official Roese-Gottlieb and modified Roese-Gottlieb tests on skimmilk  
and buttermilk.

SAMPLE	ROESE-GOTTLIEB (OFFICIAL*)	ROESE-GOTTLIEB (MODIFIED*)	VARIATION
<b>Skimmilk</b>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A2-25 .....	0.07	0.08	+0.01
A2-26 .....	0.11	0.09	-0.02
A2-27 .....	0.08	0.09	+0.01
A2-28 .....	0.09	0.10	+0.01
N3-18 .....	0.06	0.05	-0.01
N3-23 .....	0.09	0.06	-0.03
Average .....	0.083	0.078	-0.015
<b>Buttermilk</b>			
S3-30E .....	0.55	0.54	-0.01
S3-30F .....	0.56	0.57	+0.01
S3-30G .....	0.65	0.64	-0.01
S3-28B .....	0.64	0.63	-0.01
S3-28C .....	0.59	0.60	+0.01
S3-28D .....	0.65	0.65	0.00
Average .....	0.606	0.605	-0.008

\*Single determinations.

*Modified Roese-Gottlieb Method.*

Samples of the quantities recommended in the description of the official Roese-Gottlieb methods for the determination of fat in milk, cream, and butter were weighed on an analytical balance after careful preparation to insure accurate and representative portions. The reagents in quantities and order recommended in the official method were added to the samples in Mojonnier extraction flasks, and the various operations for the official Roese-Gottlieb method were carried out in these flasks, the mixture being centrifuged for a quick separation, instead of being allowed to settle out in Röhrig tubes. With skimmilk, buttermilk, and wash water, ten gram samples were used, and the tests were carried out in the same manner as for milk.

Table 3 shows the quantities of redistilled ethyl and petroleum ethers used for extracting the fat with the modified Roese-Gottlieb method.

TABLE 3.

*Quantities of redistilled ethyl and petroleum ethers used in modified Roese-Gottlieb tests.*

PRODUCT	AMOUNT OF EACH ETHER USED		
	Extractions		
	1	2	3
Milk.....	cc. 25	cc. 15	cc. ..
Cream.....	25	25	15
Butter.....	25	25	15
Skimmilk.....	25	15	.
Buttermilk.....	25	15	..
Wash Water.....	25	15	..

The solvent containing the fat was carefully poured into an aluminum dish, and evaporation of the ether was accomplished by means of an electric hot plate. The extracted fat was dried at a temperature of 266°-275° F. (130°-135° C.) under 27-29 inches of vacuum, to constant



weight, the time ordinarily required being six to eight minutes. The dried fat and the aluminum dish used as a counterpoise in weighing were brought to room temperature in a Mojonnier cooling chamber.

### *Babcock Methods.*

#### **MILK.**

Milk samples were measured with a 17.6 cc. pipet at a temperature of 115° F. (46.1° C.), cooled to a temperature of 60°–70° F. (15.5°–21.1° C.), and acid within the same range of temperature was added. The samples were centrifuged for three periods of five minutes each, or longer, with the tester running 10 to 15 per cent above the speed recommended by Farrington and Woll<sup>1</sup> for the diameter of tester used, a temperature of 130°–135° F. (54.4°–57.2° C.) being maintained on the last whirling. Tests were tempered for five minutes in a water bath at 132° F. (55.5° C.) and read two ways, (1) from the extreme bottom of the bottom meniscus to the extreme top of the top meniscus, (2) after the addition of glymol. The reading with glymol was to ascertain the volume occupied by the meniscus and to give opportunity for other comparisons. Standard eight per cent, 18-gram milk-test bottles, graduated to 0.1 per cent, were used, all of which were separately checked by two different individuals, according to the following specification: The maximum error for the total graduation, or any portion thereof, shall not exceed 0.02 of 1 per cent. Bottles not meeting this requirement were discarded.

The pipets used conformed to the specifications of the Bureau of Standards<sup>2</sup>.

#### **CREAM.**

Cream samples were heated in a water bath held at 115° F. (46.1° C.), thoroughly mixed, weighed on a sensitive moisture test scale, cooled to 60°–70° F. (15.5°–21.1° C.), and acid within the same range of temperature was added. The tester was run for three periods of five minutes each, or longer, at 10 to 15 per cent over the speed recommended by Farrington and Woll for the diameter of the tester used, a temperature of 130°–135° F. (54.4°–57.2° C.) being maintained on the last whirling. Tests were tempered five minutes at 132° F. (55.5° C.) and read shortly after the addition of glymol. Standard 50 per cent 18-gram long-neck cream-test bottles, graduated to 0.5 per cent, were used, all of which were separately checked by two different individuals, according to the following specification: The maximum error for the total graduation, or any portion thereof, shall not exceed 0.2 of 1 per cent. Bottles not meeting this requirement were discarded.

<sup>1</sup> *Testing Milk and its Products*, 24th ed., 57.

<sup>2</sup> U. S. Bur. Standards Circ. 9, 7th ed.

#### BUTTERMILK AND SKIMMILK.

Buttermilk and skimmilk samples were tested by the so-called "vigorous" method, 20-22 cc. of sulfuric acid being used and the samples being centrifuged for at least 20 minutes at 10 to 15 per cent over the speed recommended by Farrington and Woll. Regular skimmilk bottles were used.

#### BASIS OF COMPARING ROESE-GOTTLIEB AND BABCOCK TESTING.

All testing of milk, cream, and butter was done in duplicate with both the modified Roese-Gottlieb and Babcock methods. In case the duplicates did not check within a given tolerance, additional tests were made. The skimmilk, buttermilk, and wash water tests with the modified Roese-Gottlieb method were run as single determinations, after it had been ascertained how closely duplicates checked. The Babcock testing of buttermilk required many trials in some instances, because of the irregular results obtained; the highest result was recorded.

#### EFFECT OF PIPETTING MILK SAMPLES AT DIFFERENT TEMPERATURES.

To ascertain (1) the delivery of the 17.6 cc. pipet and (2) any difference in the Babcock test when milk samples are pipetted at a higher temperature, the following experiment was carried out: Twelve milk-test bottles were carefully cleaned, dried, and accurately weighed on the analytical balance. Six samples of milk, ranging from 4.05 to 6.55 per cent, were pipetted into the weighed test bottles at temperatures of 70° F. (21.1° C.) and 120° F. (48.8° C.), twenty seconds' time for emptying being allowed in each instance. Reweighing the bottles on the analytical balance gave the accurate weight of the milk delivered at the two temperatures. The average of the six Babcock tests and the weight of the milk delivered are given in Table 4.

While the error in delivery, measuring with a 17.6 cc. pipet at 120° F. (48.8° C.), is greater than at 70° F. (21.1° C.), it is apparently not enough to affect the accuracy of the Babcock test, the difference on all samples being well within the error of reading the tests. The average of the tests, measuring with a 17.6 cc. pipet at 70° F. (21.1° C.) and 120° F. (48.8° C.), is practically the same.

#### I.—INDIVIDUAL SAMPLES.

#### COMPARISON OF MILK TESTING.

Table 5 shows the relation between the modified Roese-Gottlieb and Babcock tests on milk samples. On 32 samples, the official Babcock method shows an average of practically 0.1 per cent higher than

TABLE 4.  
*Effect of temperature on delivery of pipet and on Babcock test.*

	70° F.			120° F.		
	Milk Delivered by 17.6 cc. Pipet	Babcock Test*		Milk Delivered by 17.6 cc. Pipet	Babcock Test*	
		1	2		1	2
Average of 6 tests...	17.9680 grams	per cent 4.81	per cent 4.64	17.8425 grams	per cent 4.82	per cent 4.65
Error in delivery...	-0.16%	.....	.....	-0.87%	.....	.....

\*1. Reading to extremes. 2. Reading with glymol.

TABLE 5.  
*Comparison of modified Roese-Gottlieb and Babcock tests on milk.*

SAMPLE	ROESE-GOTTLIEB (MODIFIED) TEST	BABCOCK TEST*		BABCOCK VARIATION†	
		1	2	1	2
	per cent	per cent	per cent	per cent	per cent
A2-1.....	4.92	5.0	4.81	+.08	-.11
A2-2.....	4.78	4.95	4.78	+.17	None
A2-3.....	4.93	5.05	4.90	+.12	-.03
A2-4.....	4.92	5.07	4.90	+.15	-.02
A2-5.....	4.77	4.87	4.67	+.10	-.10
A2-6.....	4.90	5.03	4.83	+.13	-.07
A2-7.....	4.83	4.87	4.67	+.04	-.16
A2-8.....	4.75	4.75	4.58	None	-.17
A2-14.....	4.76	4.85	4.70	+.09	-.06
A2-14.....	4.82	4.97	4.77	+.15	-.05
A2-15.....	4.69	4.80	4.60	+.11	-.09
A2-15.....	4.74	4.80	4.60	+.06	-.14
A2-16.....	4.69	4.75	4.58	+.06	-.11
A2-16.....	4.75	4.85	4.70	+.10	-.05
A2-17.....	4.56	4.55	4.35	-.01	-.21
A2-17.....	4.47	4.67	4.45	+.20	-.02
A2-17.....	4.45	4.55	4.38	+.10	-.07
A2-21.....	4.64	4.78	4.60	+.14	-.04
A2-21.....	4.66	4.80	4.60	+.14	-.06
A2-22.....	4.68	4.78	4.68	+.10	.....
A2-22.....	4.65	4.80	4.60	+.15	-.05
A2-23.....	4.55	4.63	4.45	+.08	-.10
A2-23.....	4.65	4.68	4.53	+.03	-.12
A2-25.....	4.53	4.61	4.41	+.08	-.12
A2-25.....	4.64	4.65	4.50	+.01	-.14
A2-26.....	4.45	4.58	4.38	+.13	-.07
A2-26.....	4.53	4.61	4.41	+.08	-.12
A2-26.....	4.42	4.51	4.31	+.09	-.11
A2-27.....	4.55	4.70	4.50	+.15	-.05
A2-27.....	4.59	4.70	4.48	+.11	-.11
A2-27.....	4.57	4.68	4.45	+.11	-.12
A2-28.....	4.62	4.65	4.50	+.03	-.12
Average.....	4.67	4.77	4.58	+.10	-.09

\*1. Reading to extremes. 2. Reading with glymol.

†+ Indicates higher than modified Roese-Gottlieb method.

†- Indicates lower than modified Roese-Gottlieb method.

the Roese-Gottlieb method. In one sample the Babcock result was equal to and in one sample it was 0.01 per cent lower than that of the Roese-Gottlieb, while in the other 30 samples the Babcock results were all higher.

Reading with glymol gave values averaging practically 0.1 per cent too low on the 32 samples.

### COMPARISON OF CREAM TESTING.

Table 6 gives the results of comparative cream testing with the Roese-Gottlieb and Babcock methods. Out of 34 tests, the Babcock method was too high in 26 cases (average of 0.26 per cent) and too low in 8

TABLE 6.

*Comparison of modified Roese-Gottlieb and Babcock tests on cream.*

SAMPLE	ROESE-GOTTLIEB MODIFIED TEST	BABCOCK TEST	VARIATION
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A2-1.....	38.23	38.50	+0.27
E2-1.....	37.36	37.50	+0.14
A2-2.....	36.70	37.00	+0.30
E2-2.....	35.35	35.20	-0.15
A2-3.....	39.01	39.25	+0.24
E2-3.....	37.65	37.50	-0.15
A2-4.....	36.86	37.00	+0.14
E2-4.....	36.12	36.50	+0.38
A2-5.....	35.79	36.13	+0.34
E2-5.....	35.00	35.50	+0.50
E2-6.....	37.97	38.00	+0.03
A2-6.....	39.32	39.50	+0.18
A2-7.....	38.64	39.00	+0.36
E2-7.....	36.98	37.12	+0.14
A2-8.....	34.01	34.00	-0.01
E2-8.....	32.87	33.25	+0.38
E2-14.....	36.85	37.25	+0.40
A2-14.....	38.43	38.50	+0.07
A2-15.....	35.95	36.00	+0.05
E2-15.....	34.69	35.00	+0.31
A2-16.....	36.81	37.00	+0.19
E2-16.....	35.72	35.50	-0.22
A2-17.....	36.27	36.20	-0.07
A2-21.....	38.40	38.50	+0.10
A2-22.....	34.61	34.75	+0.14
A2-23.....	39.16	39.30	+0.14
A2-25.....	37.11	37.25	+0.14
E2-25.....	36.33	36.75	+0.42
A2-26.....	38.83	39.00	+0.07
E2-26.....	37.71	37.50	-0.21
A2-27.....	37.49	37.30	-0.19
E2-27.....	35.68	35.90	+0.22
A2-28.....	36.94	37.00	+0.06
E2-28.....	36.26	36.00	-0.26
Average.....	36.80	36.93	+0.13

cases (average of 0.15 per cent). Taken as a whole, the Babcock test on 34 trials was 0.13 per cent too high. The difference in the two methods indicates, as in the milk testing, the variability of the Babcock test as a result of influencing factors.

#### COMPARISON OF SKIMMILK AND BUTTERMILK TESTING.

The Babcock method with skimmilk and buttermilk gave results, even with the so-called "vigorous" method, which in no way showed the actual losses in these products.

Table 7 shows the comparison of the Roese-Gottlieb and Babcock methods in determining the butterfat in skimmilk and buttermilk.

TABLE 7.  
*Comparison of modified Roese-Gottlieb and Babcock tests for butterfat on skimmilk and buttermilk.*

SAMPLE	ROESE-GOTTLIEB MODIFIED TEST	BABCOCK "VIGOROUS" TEST	BABCOCK VARIATION
<b>Skimmilk</b>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A2-1.....	0.06	0.025	-0.035
A2-15.....	0.08	0.01	-0.07
A2-2.....	0.09	0.01	-0.08
A2-16.....	0.08	0.015	-0.065
A2-3.....	0.08	0.015	-0.065
A2-4.....	0.07	0.01	-0.06
A2-5.....	0.09	0.015	-0.075
A2-6.....	0.09	0.015	-0.075
A2-7.....	0.08	0.01	-0.07
A2-8.....	0.13	0.02	-0.11
A2-25.....	0.07	0.01	-0.06
A2-26.....	0.09	0.015	-0.075
A2-27.....	0.09	0.017	-0.073
A2-28.....	0.10	0.012	-0.088
A2-14.....	0.11	0.01	-0.10
Average.....	0.087	0.014	-0.075
<b>Buttermilk</b>			
E2-1.....	0.69	0.38	-0.31
E2-2.....	0.66	0.12	-0.54
E2-3.....	0.65	0.20	-0.45
E2-4.....	0.57	0.23	-0.34
E2-5.....	0.61	0.31	-0.30
E2-6.....	0.58	0.33	-0.25
E2-7.....	0.57	0.37	-0.20
E2-8.....	0.55	0.07	-0.48
E2-14.....	0.57	0.24	-0.33
E2-16.....	0.55	0.31	-0.24
E2-25.....	0.56	0.10	-0.46
E2-26.....	0.56	0.25	-0.31
E2-27.....	0.45	0.12	-0.33
E2-28.....	0.52	0.09	-0.43
Average.....	0.571	0.223	-0.348

## SPECIFIC GRAVITY OF BUTTERFAT.

The specific gravity of the butterfat in the milk received was determined according to the official Pycnometer method, the weight at 132° F. (55.5° C.) being compared with the weight of distilled water, calculated to 4° C., the average of several determinations showing 0.8943. As Babcock test bottles are calibrated on the basis of butterfat having a specific gravity of 0.9000 at 135° F. (57.2° C.), the butterfat in the milk, with a specific gravity of 0.8943 at 132° F. (55.5° C.) might account for a Babcock test error amounting to 0.6 of a pound shortage for every 100 pounds of butterfat purchased. On the milk samples, the specific gravity of 0.8943 might account for a Babcock reading 0.02 to 0.03 per cent too high.

## II.—FACTORY CONTROL.

To obtain the comparison of the Roesse-Gottlieb and Babcock methods on milk, under actual commercial conditions, the amount of butterfat received in the form of whole milk was carefully determined by both methods, and accounted for during the process of manufacturing butter by the Roesse-Gottlieb method.

The butterfat accounting data are from work done with more care than ordinarily prevails in a creamery, but it was necessary to account for practically all the butterfat in order that proper conclusions might be deducted from the results secured.

The samples for determining the butterfat received were taken directly from the milk in the receiving vats after thorough stirring, drip samples having proved inaccurate for this work. The total of butterfat recovered from the milk and the loss in the skimmilk served as an excellent check against the total pounds of butterfat found in the milk and proved the accuracy of these basic figures.

The data shown in Table 8, giving figures for two periods and accounting for all but 0.35 per cent and 0.14 per cent, respectively, of the total pounds of butterfat received for the two periods, warrant the conclusion that any greater shortage occurring, when substituting the Babcock test on the milk received during these periods, would be due to the Babcock test showing more butterfat than was actually present. This comparison is brought out in the table where the total number of pounds of butterfat for the two periods is shown by the Babcock tests on the milk received during these periods. The fact that when using the Babcock tests of the milk, 3.10 per cent and 3.55 per cent of butterfat, respectively, is unaccounted for during the two periods, shows that the Babcock tests were too high.

TABLE 8.

*Comparison of Roese-Gottlieb (modified) and Babcock tests in factory accounting.*

PRODUCT	FEB. 1-8, 1922				FEB. 25-28, 1922			
	Roese-Gottlieb Modified Test		Babcock Test		Roese-Gottlieb Modified Test		Babcock Test	
	pounds	per cent	pounds	per cent	pounds	per cent	pounds	per cent
Whole Milk .....	3,826.2	100	3,961.9	100	1,868.4	100	1,920.9	100
Butter .....	3,707.0	96.88	.....	.....	1,806.9	96.70	.....	.....
Samples .....	7.0	.18	.....	.....	4.6	.24	.....	.....
Rinsings .....	7.1	.18	.....	.....	1.3	.06	.....	.....
Skimmilk .....	59.9	1.56	.....	.....	31.8	1.70	.....	.....
Buttermilk .....	37.8	1.00	.....	.....	15.8	.90	.....	.....
Wash Water .....	2.3	.06	.....	.....	1.0	.05	.....	.....
Unaccounted .....	5.1	.14	140.8	3.55	7.0	.35	59.5	3.10

Table 9 shows another comparison, under actual commercial conditions, of the Babcock and Roese-Gottlieb methods of testing milk on the pounds of butterfat received daily for a period of six days. The Babcock tests invariably showed more butterfat than was actually present, the average for the six-day period being 2.26 per cent of the total pounds. This figure agrees closely with the figure of 2.14 per cent, which showed, by comparison of the individual tests, that the Babcock method was in error.

TABLE 9.

*Comparison of Babcock and modified Roese-Gottlieb methods of testing milk on pounds of butterfat received.*

PERIOD	BUTTERFAT		BABCOCK SHORTAGE ON FAT SHOWN BY ROESE-GOTTLIEB MODIFIED TEST
	Roese-Gottlieb Modified Test	Babcock Test	
February	pounds	pounds	per cent
14	425.9	439.2	3.1
15	472.3	478.3	1.3
16	407.9	413.1	1.3
21	470.2	484.4	3.0
22	414.5	423.3	2.1
23	480.0	488.5	1.8
Totals...	2,670.8	2,726.8	Average..... 2.26

## SUMMARY.

A comparison of the Roese-Gottlieb and Babcock methods of testing was made, and the comparison was extended to commercial conditions in accurately accounting for the butterfat during the process of manufacturing butter from whole milk. A modified Roese-Gottlieb method which had previously been proved to agree with the official Roese-Gottlieb method was used.

A comparison of 32 milk tests, varying in fat content from 4.42 to 4.92 per cent, showed the Babcock test to be an average of 0.1 per cent high, reading from the bottom of the lower meniscus to the extreme top of the upper meniscus. This error shown in the Babcock testing of milk, reading to the extremes, amounts to a loss of 2.14 per cent of the total pounds of butterfat purchased. The testing of cream with the Babcock method gave results checking closely with those of the Roese-Gottlieb method. The average variation of 0.13 per cent high, shown by the Babcock tests in 34 samples of cream ranging from 33 to 39 per cent butterfat, is equivalent to a loss of 0.35 per cent on the total pounds of butterfat purchased, compared to 2.14 per cent loss on the total pounds of butterfat purchased in milk.

The testing of skimmilk and buttermilk, even with the so-called "vigorous" methods, gave results which in no way showed the actual fat content of these products.

The specific gravity of the butterfat in the milk was slightly low, but not sufficiently so to account for more than a small portion of the error in the Babcock milk tests.

Comparison of the Roese-Gottlieb and Babcock methods of testing milk under factory conditions, for accurate accounting of butterfat through the process of manufacturing butter from whole milk, proved the Babcock method showed more butterfat than was actually present. During two periods of several days each, when 1,868.4 and 3,826.2 pounds of butterfat, respectively, were received by the factory in the form of whole milk, all but 0.35 and 0.14 per cent, respectively, of the total pounds of butterfat received, was accounted for on the basis of the Roese-Gottlieb tests on the milk; while on the basis of the Babcock tests the unaccountable butterfat amounted to 3.10 and 3.55 per cent, respectively, of the total pounds of butterfat for the two periods.

Comparison of the daily total pounds of butterfat received for a period of six days showed the Babcock results for the period to have 2.26 per cent more butterfat than was actually present, compared to 2.14 per cent, the value computed from the error found in the 32 individual milk tests.

The results reported upon were obtained from milk and cream samples showing a narrow range of variation in butterfat, but are applicable to the conditions under which these tests were made.



## COMPOSITION OF COMMERCIAL MUSTARD BRANS WITH SPECIAL REFERENCE TO THE DETECTION OF ADDED MUSTARD BRAN IN PREPARED MUSTARD.

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Washington, D. C.).

In an investigation of the composition of commercial mustard seeds and the detection of added mustard bran in prepared mustard<sup>1</sup>, Hertwig found that (1) the nitrogen and crude fiber content of a prepared mustard is alone insufficient to detect adulteration with mustard bran in some cases; (2) that the composition of mustard brans and the ratios between certain constituents differ greatly from those of mustard seed, and these differences offer a means of detecting added bran in prepared mustards; (3) that certain ratios between the nitrogen, crude fiber, total phosphoric acid, calcium oxide, and magnesium oxide will often indicate the presence of added bran even when the crude fiber is not excessive.

These conclusions were made following the analyses of 43 commercial mustard seeds, 3 commercial mustard brans, 1 commercial mustard flour, 2 prepared mustards of known composition, and 15 commercial prepared mustards. The number of seed varieties analyzed is sufficiently large to establish the general composition of commercial mustard seeds, but the number of brans analyzed is too limited to establish that of commercial mustard brans.

Realizing that it is necessary first to know definitely the composition of commercial mustard brans in general, in order to ascertain the change in composition that prepared mustard may be expected to undergo on addition of bran, it was decided to augment the present data on the composition of commercial mustard brans. To this end, 16 samples of brans were collected for analysis from various spice mills. No information was obtainable, however, in respect to the kind of seed from which these brans were made.

The samples were ground as fine as is possible in an electrically driven Enterprise mill. The methods of analysis, with the exception of the one for crude fiber, were those used by Hertwig in the previous investigation. The crude fiber method differed only in the omission of the mortar grinding of the samples after extraction with ether. As mustard bran contains much less oil than whole seed, mill grinding reduces the bran to a finer condition; therefore, for comparative purposes with prepared mustard, the extra grinding of the defatted sample is not so essential with bran. Sample 16, with the largest crude fiber content, analyzed with and without this extra grinding, gave the following results:

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 7: 68.

	CRUDE FIBER	RATIOS				
		N C. F.	P <sub>2</sub> O <sub>5</sub> C. F.	MgO C. F.	$\frac{\text{CaO} \times \text{C. F.}}{\text{P}_2\text{O}_5 \times \text{N}}$ (A)	$\frac{\text{A}}{\text{MgO}^*}$
No extra grinding.	per cent (24.90) (25.46)	0.09	0.01	0.01	52.3	196.6
Extra grinding....	(23.59) (23.71)	0.10	0.01	0.01	49.1	184.6

\*Moisture- and fat-free basis.

Although the extra grinding slightly lowers the crude fiber results, the ratios are not materially altered. Samples with less crude fiber would be expected to be less affected in this respect.

Table 1 gives the analyses of the brans and the proposed ratios. The samples are arranged in the order of their ascending crude fiber contents.

Table 2 gives the maximum and minimum values of the constituents and ratios of 43 commercial mustard seed and 19 commercial mustard bran samples so far analyzed by the methods of this investigation.

In comparing the bran analyses with those of the seed it should be kept in mind that the bran may contain more or less of the inner seed materials.

#### DISCUSSION OF RESULTS AND CONCLUSIONS

The wide range in the results for the brans is undoubtedly due to the presence of varying amounts of the inner portions of the seed. The samples of highest crude fiber content may be safely assumed to be the freest from inside seed portions. The rise in the crude fiber values is accompanied by a regular change in the other constituents in a definite downward or upward direction. This concomitant change of values is especially evident in the ratios between various constituents.

The analyses of these commercial mustard brans justify the following previous claims made by Hertwig:

(1) The compositions of commercial mustard brans, comparatively free from inside seed materials, differ markedly from those of whole seed. The ratios given highly accentuate this difference.

(2) The proposed ratios between constituents of seed and bran are of such different magnitudes that small additions of bran to prepared mustard should make these ratios incompatible with those of seed only.

It is concluded that the proposed ratios between nitrogen, crude fiber, total phosphoric acid, calcium oxide, and magnesium oxide should be of valuable assistance to prove the presence of small quantities of added mustard bran in prepared mustard in the many instances where the crude fiber alone does not show its presence.

TABLE  
Composition of commercial  
(Averages of duplicate)

SAMPLE NUMBER	ON ORIGINAL MATERIAL								
	Moisture Vacuo 100°C.	Ether Extract	Nitro- gen	Crude Fiber	Total Ash	Acid- Insolu- ble Ash	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	7.87	15.74	4.52	10.77	5.41	0.02	1.851	1.030	0.605
2	7.29	17.89	4.33	11.96	5.47	0.30	1.636	1.053	0.573
3	7.43	17.82	3.23	13.23	4.65	0.61	1.443	0.644	0.526
4	7.99	14.03	3.18	15.01	5.43	0.31	0.782	1.375	0.302
5	8.59	15.07	3.48	15.76	5.68	0.33	1.125	1.341	0.416
6	8.68	12.84	3.71	16.52	5.35	0.08	1.233	1.141	0.422
7	8.24	18.29	3.08	17.24	4.84	0.06	1.054	1.191	0.333
8	7.93	14.00	3.04	19.37	5.13	0.10	0.926	1.288	0.311
9	8.59	11.58	2.72	19.57	5.21	0.10	0.712	1.352	0.265
10	8.09	11.71	2.77	19.54	5.05	0.10	0.747	1.352	0.263
11	9.36	8.87	2.61	19.92	4.29	0.05	0.586	1.435	0.275
12	10.56	10.97	2.80	20.83	5.06	0.17	0.740	1.301	0.320
13	9.01	10.69	2.67	21.27	5.19	0.14	0.691	1.394	0.293
14	6.82	10.79	2.66	21.37	5.22	0.19	0.702	1.366	0.290
15	9.23	8.47	2.53	22.29	5.10	0.09	0.572	1.518	0.314
16	9.63	5.86	2.28	25.18	5.20	0.04	0.341	1.614	0.225

\*On moisture- fat-free basis.

TABLE 2.

Maximum and minimum values of analyses and ratios of commercial mustard seeds and commercial mustard brans.

ON MOISTURE- AND FAT-FREE BASIS						RATIOS					
	Nitro- gen	Crude Fiber	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	$\frac{N}{C.F.}$	$\frac{P_2O_5}{C.F.}$	$\frac{MgO}{C.F.}$	$\frac{CaO}{MgO}$	$\frac{CaO \times C.F.}{P_2O_5 \times N}$	$\frac{(A)}{MgO^*}$
Seeds* (43 samples)											
Maximum..	<i>per cent</i> 8.35	<i>per cent</i> 11.10	<i>per cent</i> 4.40	<i>per cent</i> 1.734	<i>per cent</i> 1.326	1.00	0.49	0.16	1.71	0.78	0.88
Minimum...	6.42	7.20	2.28	0.734	0.616	0.56	0.28	0.07	0.79	0.26	0.21
Brans (19 samples)											
Maximum..	5.92	29.2	2.42	1.910	0.792	0.42	0.17	0.06	7.2	52.3	196.6
Minimum...	2.70	14.1	0.40	0.862	0.266	0.09	0.01	0.01	1.2	1.3	1.6

\*Fat- (acid insoluble ash) free solids basis.

1.

*mustard brans.*

determinations.)

ON MOISTURE- AND FAT-FREE BASIS					RATIOS					
Nitro- gen	Crude Fiber	Total P <sub>2</sub> O <sub>5</sub>	CaO	MgO	$\frac{N}{C. F.}$	$\frac{P_2O_5}{C. F.}$	$\frac{MgO}{C. F.}$	$\frac{CaO}{MgO}$	$\frac{CaO \times C. F.}{P_2O_5 \times N}$	$\frac{(A)}{MgO^*}$
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>						
5.92	14.1	2.42	1.348	0.792	0.42	0.17	0.06	1.7	1.3	1.6
5.79	16.0	2.19	1.407	0.766	0.36	0.14	0.05	1.8	1.8	2.3
4.32	17.7	1.93	0.862	0.704	0.24	0.11	0.04	1.2	1.8	2.6
4.08	19.0	1.00	1.763	0.387	0.21	0.05	0.02	4.6	8.3	21.4
4.56	20.6	1.47	1.757	0.545	0.23	0.08	0.03	3.2	5.1	9.4
4.73	21.0	1.57	1.454	0.538	0.22	0.07	0.02	2.7	4.1	7.6
4.19	23.5	1.43	1.621	0.453	0.18	0.06	0.02	3.6	6.3	13.9
3.89	24.8	1.19	1.650	0.398	0.16	0.05	0.02	4.1	8.9	22.4
3.41	24.5	0.89	1.693	0.332	0.14	0.04	0.01	5.1	13.7	41.3
3.45	24.4	0.93	1.686	0.328	0.14	0.04	0.01	5.1	12.8	39.0
3.19	24.4	0.72	1.755	0.336	0.13	0.03	0.01	5.2	10.2	30.4
3.57	26.5	0.94	1.658	0.408	0.13	0.04	0.01	4.1	13.1	32.1
3.32	26.5	0.86	1.736	0.365	0.12	0.03	0.01	4.8	16.1	44.1
3.23	25.9	0.85	1.658	0.352	0.12	0.03	0.01	4.7	15.6	44.3
3.07	27.1	0.69	1.844	0.381	0.12	0.03	0.01	4.9	23.4	61.4
2.70	29.2	0.40	1.910	0.266	0.09	0.01	0.01	7.2	52.3	196.6



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## ROY WILSON HILTS

Roy Wilson Hiltz was born in McLean County, Illinois, on November 9, 1879. He died in San Francisco on January 12, 1924. At the time of his death he was Chief of the Western Food and Drug Inspection District, one of the three administrative field divisions of the Bureau of Chemistry enforcing the Federal Food and Drugs Act.

Mr. Hiltz' connection with the Bureau of Chemistry began in 1907, the year the Food and Drugs Act became effective. He was graduated from the University of Illinois in 1904; some of his undergraduate work, however, had been done at the University of Colorado and at Leland Stanford University. His entry into the Federal service followed a three-year period as a chemist in commercial employ. He not only made for himself a reputation as a skilful and accurate analyst and investigator, but he demonstrated the possession of qualities of leadership, and his advancement was rapid. After preliminary service in the Chicago and Philadelphia Laboratories of the Bureau of Chemistry he served successively as the head of the Galveston, New Orleans, Seattle, and San Francisco Laboratories, and was appointed Chief of the Western District on October 1, 1917. He was married on October 30, 1923. Mr. Hiltz never fully recovered from an attack of influenza suffered several years ago, although he had carried on his official work with his usual efficiency and energy. This attack, however, resulted in a serious heart affection, which was the ultimate cause of his untimely death.

Although the needs of the service and continued advancement led him into administrative lines in which he showed the highest proficiency, Mr. Hiltz' instincts were always those of the analyst and scientific investigator. To the day of his death, despite the duties of an exacting executive position, he kept in touch with the scientific work of the laboratories under his direction and gave to it the benefit of his personal attention and supervision. He constantly encouraged the younger chemists of his organization to carry on investigative work and was never too busy to aid them in the planning and presentation of such work.

Mr. Hiltz' connection with the Association of Official Agricultural Chemists began with his entrance into the Government service. His name first appears in the proceedings of the 25th convention, in 1908, as a collaborator on cocoa products and on flavoring extracts. From that time he contributed to the association at frequent intervals as collaborator, referee, or author. His last contribution was his report as referee on "The Determination of Moisture in Dried Fruit", which appeared in the last issue of this Journal. Although in recent years his location on the Pacific coast made attendance at the meetings of the association impracticable, his interest was maintained; this is indicated not only by his own contributions, but by those of members of his district working under his stimulus and direction.

What goes before is a matter of written record. The other record—the one that will remain impressed upon the memories and hearts of his friends—can not so well be written; it is that of an able and energetic worker, a wise counselor, a loyal friend, a courteous gentleman. No thought of personal comfort or gain ever swerved him from the straight course of duty. He never spared himself, and his untimely death was undeniably hastened by his determination to do the work at hand. No more fitting

tribute can be paid to Mr. Hilts than that contained in the following words, which are those of one who was closely associated with him for many years by the ties of official work and the bonds of friendship:

His was the finest character I have ever known; his friendship, a delight, a guide, and an inspiration. While every inch and fiber a man he was as gentle, kind, and susceptible to the finer emotions as any woman. He was proud, with the unconscious pride of a thoroughbred. No man was more utterly forgetful of self, or more considerate of others of all degree. Hypocrisy, malice, envy, sloth—these traits were so foreign to his nature and to his scheme of things that for him they simply did not exist. Being a very human being, he had his personal likes and dislikes and, perhaps, even prejudices. His passionate regard for justice and essential truth, however, was something far above all else, and he dealt with each and every problem fairly and considerately beyond belief. So with every other phase of his work and, it goes without saying, of his life. His great mind and fine spirit must and will carry on, relieved at last of that frail body to which to the end he would concede nothing, holding duty and service above all else.

In the words of the Secretary of Agriculture: "He leaves a most enviable record for service for the Department of Agriculture, and his untimely passing is an irreparable loss".

P. B. DUNBAR.

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PROCEEDINGS OF THE THIRTY-NINTH ANNUAL  
CONVENTION OF THE ASSOCIATION OF  
OFFICIAL AGRICULTURAL  
CHEMISTS, 1923.

The thirty-ninth annual convention of the Association of Official Agricultural Chemists was held at the Raleigh Hotel, Washington, D. C., November 19-21, 1923.

The meeting was called to order by the President, A. J. Patten, Agricultural Experiment Station, E. Lansing, Mich., on the morning of November 19, 1923, at 10 o'clock.

OFFICERS, COMMITTEES, REFEREES, AND ASSOCIATE  
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SUBCOMMITTEE B: E. M. Bailey (1924), (Agricultural Experiment Station, New Haven, Conn.), *Chairman*; H. C. Lythgoe (1926); A. G. Murray (1928). [Spices and other condiments, limit of accuracy in the determination of small amounts of alcohol, testing chemical reagents, naval stores, drugs (acetylsalicylic acid, alcohol in drugs, arsenicals, phenylcinchoninic acid, barbital and phenol-barbital, camphor and monobromated camphor, chaulmoogra oil, chloramine-T products, chloroform and chloral hydrate, ipecac alkaloids, radio activity in drugs and water, laxatives and bitter tonics, mercurials, methylene blue, papain, phenolphthalein, pyramidon, separation of quinine and strychnine, silver proteinates).]

SUBCOMMITTEE C: W. C. Geagley (1924), (State Food and Drug Department, Lansing, Mich.), *Chairman*; R. E. Doolittle (1926); C. F. Whitney (1928). [Dairy products (moisture in cheese, fat in malted and dried milk), fats and oils, baking powders and baking chemicals (fluorides in baking powder), eggs and egg products (liquid and frozen eggs, dried eggs, zinc in dried eggs), food preservatives, coloring matters in foods, metals in foods (arsenic), fruits and fruit products (pectin in jams, jellies, and preserves, fruit acids), canned foods, vinegars, flavors and non-alcoholic beverages, meat and meat products (separation of meat proteins), gelatin, cereal foods (moisture, ash, chlorine in bleached flour, glutenin in flour, methods for sampling flour), cacao products (microscopical methods, crude fiber, cacao butter).]

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*Potash:*

*Associate referee:* A. P. Kerr, Agricultural Experiment Station, Baton Rouge, La.

*Phosphoric acid:*

*Associate referee:* R. B. Deemer, Bureau of Plant Industry, Washington, D. C.

*Plants:*

*General referee:* A. J. Patten, Agricultural Experiment Station, East Lansing, Mich.

*Sulfur and potash:*

*Associate referee:* W. L. Latshaw, Agricultural Experiment Station, Manhattan, Kans.

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*Acidity values of soils:*

*Associate referee:* P. S. Burgess, Agricultural Experiment Station, Kingston, R. I.

*Liming materials:*

*Associate referee:* W. M. Shaw, Agricultural Experiment Station, Knoxville, Tenn.

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*Feeding stuffs:*

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*Linseed meal:*

*Associate referee:* M. R. Coe, Bureau of Chemistry, Washington, D. C.

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*Associate referee:* H. E. Gensler, Department of Agriculture, Harrisburg, Pa.

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*Maltose products:*

*Associate referee:* F. W. Reynolds, Bureau of Chemistry, Washington, D. C.

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*General referee:* W. W. Randall, State Department of Health, Baltimore, Md.

*Coloring matters in foods:*

*General referee:* C. F. Jablonski, 641 Washington Street, New York, N. Y.

*Metals in foods:*

*General referee:* W. F. Clarke, Bureau of Chemistry, Washington, D. C.

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*Associate referee:* R. M. Hann, Bureau of Chemistry, Washington, D. C.

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*Associate referee:* H. J. Wichmann, U. S. Food and Drug Inspection Station,  
Denver, Colo.

*Fruit acids:*

*Associate referee:* E. K. Nelson, Bureau of Chemistry, Washington, D. C.

*Canned foods:*

*General referee:* A. L. Sullivan, State Department of Health, Baltimore, Md.

*Cereal foods:*

*General referee:* Raymond Hertwig, Bureau of Chemistry, Washington, D. C.

*Moisture:*

*Associate referee:* G. C. Spencer, Bureau of Chemistry, Washington, D. C.

*Ash:*

*Associate referee:* C. E. Mangels, Agricultural Experiment Station, Agricultural College, N. D.

*Chlorine in bleached flour:*

*Associate referee:* Armin Seidenberg, Department of Health, New York, N. Y.

*Glutenin in flour:*

*Associate referee:* Paul F. Sharp, Agricultural Experiment Station, Bozeman, Mont.

*Methods for sampling flour:*

*Associate referee:* G. J. Morton, U. S. Appraiser's Stores, Sansome and Washington Sts., San Francisco, Calif.

*Limits of accuracy in the determination of small amounts of alcohol:*

*General referee:* H. C. Lythgoe, State Department of Public Health, Boston, Mass.

*Vinegars:*

*General referee:* H. A. Lepper, Bureau of Chemistry, Washington, D. C.

*Flavors and non-alcoholic beverages:*

*General referee:* J. W. Sale, Bureau of Chemistry, Washington, D. C.

*Meat and meat products:*

*General referee:* R. H. Kerr, Bureau of Animal Industry, Washington, D. C.

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*Associate referee:* W. W. Ritchie, University of Missouri, Columbia, Mo.

*Gelatin:*

*General referee:* E. H. Berry, 1625 Transportation Building, Chicago, Ill.

*Eggs and egg products:*

*General referee:* Raymond Hertwig, Bureau of Chemistry, Washington, D. C.

*Liquid and frozen eggs:*

*Associate referee:* L. M. Hitchcock, 1625 Transportation Building, Chicago, Ill.

*Dried eggs:*

*Associate referee:* J. C. Palmer, U. S. Appraiser's Stores, Sansome and Washington Sts., San Francisco, Calif.

*Zinc in dried eggs:*

*Associate referee:* W. E. Kirby, 641 Washington St., New York, N. Y.

*Dairy products:*

*General referee:* Julius Hortvet, State Dairy and Food Commission, St. Paul, Minn.

*Moisture in cheese:*

*Associate referee:* L. C. Mitchell, Room 204 Old Custom House, St. Louis, Mo.

*Fat in malted milk and dried milk:*

*Associate referee:* J. T. Keister, Bureau of Chemistry, Washington, D. C.

*Fats and oils:*

*General referee:* G. S. Jamieson, Bureau of Chemistry, Washington, D. C.

*Spices and other condiments:*

*General referee:* R. E. Andrew, Agricultural Experiment Station, New Haven, Conn.

*Cacao products:*

*General referee:* E. M. Bailey, Agricultural Experiment Station, New Haven, Conn.

*Microscopical methods:*

*Associate referee:* V. A. Pease, Bureau of Chemistry, Washington, D. C.

*Crude fiber:*

*Associate referee:* E. R. Miller, U. S. Appraiser's Stores, Christopher and Washington Sts., New York, N. Y.

*Cacao butter:*

*Associate referee:* W. F. Baughman, Bureau of Chemistry, Washington, D. C.

***Baking powders and baking chemicals:***

*General referee:* L. H. Bailey, Bureau of Chemistry, Washington, D. C.

***Fluorides in baking powder:***

*Associate referee:* J. K. Morton, Bureau of Chemistry, Washington, D. C.

***Testing chemical reagents:***

*General referee:* G. C. Spencer, Bureau of Chemistry, Washington, D. C.

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***Drugs:***

*General referee:* A. E. Paul, 1625 Transportation Building, Chicago, Ill.

***Acetylsalicylic acid:***

*Associate referee:* C. W. Harrison, Food and Drug Inspection Station, Park Avenue Building, Baltimore, Md.

***Alcohol in drugs:***

*Associate referee:* E. V. Lynn, University of Washington, Seattle, Wash.

***Arsenicals:***

*Associate referee:* C. K. Glycart, 1625 Transportation Building, Chicago, Ill.

***Phenyleinchroninic acid:***

*Associate referee:* William Rabak, 311 Federal Office Building, Minneapolis, Minn.

***Barbital and phenol-barbital:***

*Associate referee:* C. K. Glycart, 1625 Transportation Building, Chicago, Ill.

***Camphor and monobromated camphor:***

*Associate referee:* A. E. Paul, 1625 Transportation Building, Chicago, Ill.

***Chaulmoogra oil:***

*Associate referee:* L. E. Warren, 535 N. Dearborn St., Chicago, Ill.

***Chloramine-T products:***

*Associate referee:* W. H. Heath, Federal Building, Buffalo, N. Y.

***Chloroform and chloral hydrate:***

*Associate referee:* H. O. Moraw, 1625 Transportation Building, Chicago, Ill.

***Ipecac alkaloids:***

*Associate referee:* A. R. Bliss, Jr., College of Medicine, Dept. of Pharmacology, University of Tennessee, Memphis, Tenn.

***Radio activity in drugs and water:***

*Associate referee:* J. W. Sale, Bureau of Chemistry, Washington, D. C.

***Laxatives and bitter tonics:***

*Associate referee:* H. C. Fuller, Industrial Research Laboratories, 1845 B St., N W., Washington, D. C.

***Mercurials:***

*Associate referee:* G. C. Spencer, Bureau of Chemistry, Washington, D. C.

***Methylene blue:***

*Associate referee:* To be appointed.

*Papain:*

*Associate referee:* L. J. Schwartz, U. S. Appraiser's Stores, Christopher and Washington Sts., New York, N. Y.

*Phenolphthalein:*

*Associate referee:* Samuel Palkin, Bureau of Chemistry, Washington, D. C.

*Pyramidon:*

*Associate referee:* A. W. Hanson, 1625 Transportation Building, Chicago, Ill.

*Separation of quinine and strychnine:*

*Associate referee:* F. L. Elliott, U. S. Appraiser's Stores, 408 Atlantic Avenue, Boston, Mass.

*Silver proteinates:*

*Associate referee:* E. O. Eaton, U. S. Appraiser's Stores, Sansome and Washington Sts., San Francisco, Calif.

Other associate referees for special work in drugs may be appointed by the general referee.

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PRESIDENT'S ADDRESS<sup>1</sup>.

## COLLOID CHEMISTRY IN RELATION TO AGRICULTURE.

By A. J. PATTEN (Agricultural Experiment Station,  
E. Lansing, Mich.).

In 1861 Thomas Graham first emphasized the fundamental distinction between colloids and crystalloids, which he recognized as a difference in the rate of diffusion. Substances that diffused slowly were usually in a non-crystalline or gelatinous form, and for that reason Graham called them "colloids" after the Greek word for glue (*Kolla*), because of their resemblance to that substance. Substances that diffused rapidly he called crystalloids, because many of them produced crystals more or less readily. This distinction between colloids and crystalloids Graham believed to be fundamental and due to some molecular condition. This distinction, however, is not fundamental and has been dropped, for it is now well known that a colloid need not be amorphous, and a colloidal state rather than a colloidal substance is the more proper term. According to Bancroft, "we may call any phase colloidal when it is sufficiently finely divided or dispersed, without committing ourselves definitely as to what degree of subdivision is necessary in any particular case".

The distinction between colloids and crystalloids is, nevertheless, very definite. In all probability, all substances may be made to assume the colloidal state. Ice is commonly regarded as a crystalloid; yet we may obtain a colloidal solution of ice in chloroform by saturating the latter with water, then suddenly cooling it in a freezing mixture. The particles of ice thus formed are so small that they remain in suspension in the chloroform indefinitely; yet they are large enough to give the liquid a slightly milky appearance. Common salt and many other inorganic substances, ordinarily seen in crystalline form, may also be obtained in colloidal solution if they are produced by chemical reactions in the midst of organic liquids in which they are insoluble. Conversely, many substances commonly regarded as colloids, such as egg albumen, may be obtained in crystalline form, if proper precautions are taken.

Accordingly, a colloid is not a substance of a particular chemical class, but rather it is one having a tendency to assume a particular physical state—a state in which it is subdivided to form particles of extremely small size, which are dispersed or scattered through a second material.

Deming<sup>2</sup> has dramatically stated the relationship of colloids to life processes in these words:

<sup>1</sup> Presented Tuesday morning, November 20, as special order of business for 11 o'clock.

<sup>2</sup> General Chemistry, 1923, p. 341.

"To realize the overwhelming importance of colloids, one need but pause to consider that all the phenomena of life are connected with processes that take place only in colloidal matter. A seed is planted in the ground, and straightway there begins a contest for water between seed and soil. In this contest the seed wins, draws water into itself, and swells up until the seed-coat bursts. Here is a process that could never take place with crystalline material.

"Presently growth begins. Little by little the stores of colloidal food-stuffs in the seed—starch, protein, and fatty substances—are acted upon by enzymes, themselves of colloidal nature. Thus these reserves of food are converted into sugar and other crystalline material, transported in this form to the growing stem or rootlet, and there rebuilt in colloid form. Soon the young shoot bursts from the soil and unfolds its leaves to the sunlight. We then behold a new marvel—photosynthesis—the building up of starch, a complex colloidal material, from two simple crystalloids, water and carbon dioxide. Thus the plant grows, becomes a tree, and after many years brings forth fruit after its kind. Roots, trunk, branches, leaves, bark, and fruit all consist of colloidal substances, with nowhere any other crystalloid than water, if we except a few simple substances such as sugar and organic acids, which form no necessary part of the plant, and destined in proper time to be itself elaborated into colloidal living tissue.

"Nor are plants alone thus intimately related to the properties of colloids. Every individual animal is built up of complex material called protoplasm, which contains many different chemical substances, and assumes many different forms. But whether this protoplasm belongs to amoeba or to man, it is essentially colloidal."

In the industries many important processes are based upon colloid chemistry. It will only be necessary to call to your minds, very briefly, a few cases. Take, for example, the flotation process adapted to the purification of ores. It is claimed that more than 60,000,000 tons of ore are treated annually by this method. The enormous rubber industry in this country is daily applying the principles of colloid chemistry. The manufacture of varnishes, paints, and pigments is essentially a colloid industry; likewise the ceramic industry deals with colloid material. During the late war our soldiers were protected from the destructive poison gases of the enemy through the application of the principles of colloid chemistry.

In the field of dairy chemistry colloid phenomena and problems are much involved. Milk contains substances that are inherently colloidal in nature, namely, casein and albumen, and also substances that behave as colloidal systems by virtue of their fine state of subdivision—that is, the fat present as emulsion, the cell-content of milk, and the enzymes.

The colloid chemistry of milk chiefly centers around the phenomenon of "protection", the protective action of lact-albumin on casein.

It has long been known that infants can digest human or asses' milk much more readily than cows' milk. Jacobi<sup>1</sup> states that "asses' milk has always been recognized as a refuge in digestive disorders, when neither mothers' or cows' milk, or its mixtures, were tolerated".

The ratio of albumen to casein in cows' milk is approximately 1 to 6, while in human milk it is 1 to 0.8 and in asses' milk it is 1 to 0.4.

Human milk is not coagulated to any extent by acids or salts, but the reverse is true with cows' milk. Hence, in the infant's stomach, cows' milk does not take up much of the acid of the gastric juice and soon coagulates in large masses. Human milk, on the contrary, takes up a large amount of acid of the gastric juice and coagulates late in small masses. The larger amount of albumen in human milk acts as a protective colloid to the casein. Cows' milk can be made to resemble human or asses' milk in protective qualities by the addition of such colloidal substances as gelatin or barley water.

The fat present in milk is carried down by the curd. The greater the extent of coagulation, the larger is the amount of fat carried down with the curd, and since such fatty curds tend to coalesce and give rise to large masses, which are only slightly affected by the digestive juices, it follows that the protective action of the albumen on the casein is an important factor.

In the manufacture of ice cream gelatin is used as a protective colloid to prevent the formation of coarse crystals and give to the cream a smoother and finer texture. More recently calcium saccharate has been used for the same purpose.

In the manufacture of spray materials fineness of division is an important factor, since the finer a suspended material is divided the more evenly can it be spread over the surface of the sprayed material. Casein and other substances have been added to lead arsenate as protective colloids to prevent the quick settling of the material during the process of spraying. Recently Hooker<sup>2</sup> has reported experiments with colloidal copper hydroxide as a fungicidal spray. He shows that it is effective for apple scab and apple blotch at a concentration of 1 part to 5,000 parts of water. This is a much smaller proportion of copper hydroxide than is used in ordinary Bordeaux mixtures.

It has been said that no manufacturer is less aware of the chemical problems underlying his trade than the master baker. His ability to feel, taste, and smell the ingredients is to him a surer guide in the production of good bread than the knowledge obtained by the use of test tubes and the balance.

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<sup>1</sup> *J. Am. Med. Assoc.*, 1908, 51: 1216.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1923, 15: 1177.



Nevertheless, there are many complex problems fundamental in the baking industry that must be solved before it can be placed on the same basis with other chemically controlled industries. The saturation and swelling of the starch granules; the production of hydrated forms of gluten; biological changes and the occlusion of gas during the growth of yeast; the working of the dough to secure elasticity; proteolytic enzyme action and the hardening action of salt on the gluten; and the changes, physical and chemical, during cooling and aging, which bring about staleness, are problems that need to be solved. Some of these have received considerable attention and are gradually being solved through the aid of colloid chemistry.

Agricultural chemists have been slow to recognize that colloids play any part in soil work. For years soils have been regarded as crystalloidal mineral material mixed with certain soluble salts and organic matter. It has been impossible, however, satisfactorily to explain certain soil phenomena on the old basis.

Van Bemellen<sup>1</sup> was the first to demonstrate the unsoundness of the old views. It had long been known that soil possessed the remarkable property of adsorbing certain soluble substances from solutions: ammonia was taken from ammonium sulfate solution, potash from potassium sulfate, and so on. It was this property that justified the use of soluble salts as artificial fertilizers. The first explanation was offered by Way<sup>2</sup>, who supposed that the process was a simple chemical reaction of the double decomposition type, and he assumed the existence in the soil of a series of reactive silicates in order to account for the observed phenomena. Subsequent writers, adopting the simple expedient of keeping away from the soil, elaborated the properties of these double silicates; and when at a later date mineralogists directed attention to the zeolites, some of the agricultural chemists assumed that these substances existed in quantity in the soil and were the reactive constituents in question.

Shortly after Way had offered his chemical hypothesis Liebig<sup>3</sup> advanced a physical explanation. He supposed that soil had some power of attracting dissolved salts similar to the power possessed by charcoal for condensing gases. Only the substances physically held in the soil were considered of immediate value to the plant, although the chemically combined substances might be a reservoir in maintaining supplies.

Further investigations showed that neither explanation was quite sufficient; Knop<sup>4</sup>, therefore, combined the two hypotheses and explained the adsorption of acids as a chemical combination with iron or aluminum oxides, and the removal of bases partly as a physical attrac-

<sup>1</sup> *Landw. Vers.-Sta.*, 1888, 35: 67.

<sup>2</sup> *J. Roy. Agr. Soc.*, 1850, 11: 313.

<sup>3</sup> *Natural Laws of Husbandry*, 1863.

<sup>4</sup> *Lehrbuch der Agrikultur Chemie*, 1863.

tion and partly as a chemical combination with silica or double aluminum silicates. But the compromise was not very satisfying and aroused little enthusiasm. Moreover, it did not help to account for the ever increasing number of apparently abnormal phenomena.

Later on van Bemellen proved that the phenomena were precisely similar to those shown by colloids and argued that the soil must be treated as a colloid. Van Bemellen did not at once arrive at the colloid explanation; he first accepted Way's chemical explanation, and, indeed, devised a method for estimating the double silicates present. Later, however, he made extensive studies of adsorption of simple gels, silica, alumina, ferric hydroxide, tin hydroxide, etc., and found it closely to resemble adsorption by soils. Other studies of colloids were made, and in each case the similarity to soil phenomena was so close as to leave no doubt that soil was essentially a colloid and soil adsorption simply a manifestation of its colloidal properties.

According to van Bemellen, who made a very exhaustive study, the following colloidal materials may function in soils: Partially decayed remains of plant and animal tissue; colloidal iron, aluminum, and silica; and colloidal silicates formed through weathering.

The absorptive capacity of any particular soil for gases, water, or salts in solution, under any particular condition, depends on the texture of the soil, and on the time during which action is allowed to take place. Parker<sup>1</sup> has shown that adsorption increases with the fineness of the texture, indicating that the heavier the soil, the greater is the amount of material possessing the power of fixation.

It is generally considered that adsorption by the soil is selective, in that the base of an electrolyte is adsorbed while the acid ion is left in solution. Many data have been presented in support of this view. It must be remembered, however, that in the soil there is a very complex material, and until the phenomena of adsorption are more clearly understood, it will be difficult to interpret the results correctly in every case.

E. J. Miller, working in the writer's laboratory, has been studying the phenomena of adsorption with activated, ash-free sugar charcoal. His results have led him to the conclusion that adsorption is hydrolytic, at least in part, and that either the basic or acid ion may be adsorbed, depending upon the selective power of the colloidal material. This view is directly opposed to that held by Michaelis and Rona, Odén, and others who have maintained that there is but one form of adsorption, and that the anion and cation are removed in equivalent amounts.

Miller has been able to show that the conclusions reached by these investigators are obtained only when working with impure charcoals

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<sup>1</sup> *J. Agr. Research*, 1913, 1: 179.

that have been treated previously with acid or that contain a large percentage of ash. It is probable that the colloidal material of the soil would behave more nearly like the impure charcoal than the ash-free charcoal used by Miller, in that its adsorptive capacity for the acid ion is already satisfied, and that acid would be set free upon the addition of a neutral electrolyte.

Some interesting results have been obtained by Miller on the relative adsorption of acids and bases by ash-free charcoal; a marked selective adsorption for various groups of acids and bases is shown. As a rule, the organic acids were adsorbed to a greater extent than the inorganic acids. The strong inorganic bases, however, were not adsorbed at all.

Gordon and his co-workers<sup>1</sup> have been carrying on some interesting work on the adsorption and replacement of plant food by colloidal oxides of iron and aluminum. They found that nitrates were adsorbed only to a very slight extent, but sulfates, and particularly the phosphates, suffered large adsorption. The order of the adsorption of the cations is calcium, magnesium, and potassium, while the order of the adsorption of the anions is phosphate, sulfate, and nitrate.

The same investigators also studied the availability of adsorbed phosphates. Colloidal ferric oxide and alumina were prepared, allowed to adsorb the maximum amount of a 0.05N solution of potassium acid phosphate, and washed until the filtrate gave no test for the phosphate. These prepared colloids were then mixed with sand in jars, and sweet potato seedlings were planted in them. The results showed that the adsorbed phosphate was available as plant food.

Soil acidity is, probably, a manifestation of the colloidal property of soils, and although it without doubt has been investigated more than any other one soil problem no one has yet been able to offer a satisfactory proof or denial of this assertion. The early investigators believed it to be due to an accumulation in the soil of complex insoluble organic acids. This view has recently been supported by Odén, who used electrometric methods on soils high in organic matter. This fails, however, to explain the acidity—in some cases high—of soils that are extremely low in organic matter. The selective adsorption theory of soil acidity was advanced by Cameron<sup>2</sup> and supported by Harris<sup>3</sup>, Parker<sup>3</sup>, and others, but has not received general recognition. Loew<sup>4</sup>, working with Porto Rican soils very low in organic matter, believes the acidity to be due to a very highly complex aluminosilicic acid to which he has given the name, "argillic acid". Bradfield<sup>5</sup> attempts to show that the acidity of colloidal clay is due to the presence of a colloidal acid.

<sup>1</sup> *Soil Science*, 1923, 15: 164, 371.

<sup>2</sup> *J. Phys. Chem.*, 1910, 14: 400.

<sup>3</sup> *Mich. Tech. Bull.*, 19: 1914.

<sup>4</sup> *Porto Rico Agr. Exp. Sta. Bull.* 13: 1913.

<sup>5</sup> *J. Am. Chem. Soc.*, 1923, 45: 2669.

The various methods proposed for determining the so-called lime requirement of soils, where the soil is treated with a neutral salt solution, can not be considered as measuring the true acidity. For, while the neutral salt solution probably does displace some of the adsorbed acid, the displacement is by no means complete. Furthermore, the soil colloids may exert a selective adsorption for the electrolyte itself, or there may be an exchange of base between the electrolyte and some of the soil compounds. Moreover, in all methods based upon the extraction of a soil with solutions of salts of weak acids there is considerable obscuring or displacement of the end point of the titration by the buffer action of the salts. When acid-treated charcoal is added to a neutral electrolyte some of the adsorbed acid is displaced from the charcoal, and some of the electrolyte takes its place. This appears to be what takes place in the soil, but, of course, one can not reason that because certain results are obtained with charcoal similar results should be forthcoming with soils, as they are two very different systems. However, it is interesting to note that the phenomena in the two cases present many things in common.

Cameron<sup>1</sup> attempts to explain the reddening of blue litmus paper when it is brought in contact with an acid soil on the basis of selective adsorption. He believes that the soil exerts a greater adsorptive power for the base of the litmus dye than the paper, and consequently with the removal of the basic ion of the dye the paper must turn red. It is very doubtful, however, if this is the correct interpretation of the phenomenon. From results obtained by Miller, as yet unpublished, it appears that the reddening of the litmus paper is a result of the reaction between the adsorbed acid and the litmus dye.

If acidity of the soil is due to the presence of adsorbed acids it should be possible to extract them and actually identify them. That this is a possibility, which will be realized in the near future through the medium of colloid chemistry, is confidently believed.

In the early studies of the water relationships of soils, the soil was treated as a mass of sand, and the distribution of water was considered solely as a surface-tension phenomenon. The conclusions reached from such investigations were not wholly in accord with facts. Keen<sup>2</sup> has shown that the relationship of water to soil is quite different from the relationship of water to sand. The evaporation of water from sand, silt, china-clay, and ignited soil proved to be relatively simple and could be explained by the known laws of evaporation and diffusion. But the evaporation of water from soil could not: it was more complex. The difference was traced to the soil colloids, and it disappeared when the soil was heated and the colloidal properties destroyed.

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<sup>1</sup> *J. Phys. Chem.*, 1923, 14: 400.

<sup>2</sup> *J. Agr. Sci.*, 1914, 9: 456.

Bouyoucos<sup>1</sup> has classified soil water as follows:

Gravitational water

Free water

Unfree water  $\left\{ \begin{array}{l} \text{capillary—adsorbed} \\ \text{combined} \left\{ \begin{array}{l} \text{water of solid solution, or} \\ \text{water of hydration.} \end{array} \right. \end{array} \right.$

He has also presented results tending to show that the amount of water that soils are able to render unfree does not vary with the different moisture contents, but that it appears to remain constant. This would seem to indicate that the ability of a soil to render water unfree is a manifestation of its colloidal state.

While it may seem from the foregoing that we are of the opinion that all phenomena are explainable on the basis of colloid chemistry, this view is not held. It is our belief, however, that the solution of many of the problems that have been baffling the agricultural chemist for generations will be found through the application of colloid chemistry. It is a hopeful sign that so many investigators who are dealing with agricultural problems are turning to this branch of the science.

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<sup>1</sup> *Soil Science*, 1921, 11: 255.

## ORDER OF PUBLICATION.

The order of publication adopted last year will be followed this year. The reports of the committees, presented on the last day of the annual meeting, will be given at the beginning of the proceedings rather than in their chronological order. This will assist the referees, associate referees, and collaborators in planning and developing their year's work. The remainder of the proceedings will then follow in the usual order.

## THIRD DAY.

### WEDNESDAY—MORNING SESSION.

#### REPORT OF COMMITTEE ON EDITING METHODS OF ANALYSIS.

The association at the 1922 meeting approved the plan submitted by the Committee on Editing Methods of Analysis for a revision of the *Book of Methods*. This plan provided that the revised edition should be of the same general form as the present book, the revision to consist principally in the deletion of methods dropped by the association and the incorporation of new methods and of additions and changes made since the last revision, including the deletions, new methods, additions, and changes made at the meeting this year, the revised book to be ready for distribution on or about July 1, 1924. The committee is pleased to report that this work has progressed satisfactorily, and unless some unforeseen delay occurs the manuscript for the revised chapters will be ready for the printer within a few months after the adjournment of this meeting.

In carrying out the revision, the committee adopted the plan of cooperating as closely as possible with the referees and associate referees in considering deletions, additions, and changes and in bringing pending methods before the association for final action. In other words, where questions concerning the deletion of methods or the incorporation of new methods, additions, and changes arose these were taken up, wherever possible, with the appropriate referee or associate referee in order that they should receive proper consideration not only by the referee but, wherever necessary, through his report by Sub-committees A, B, and C and the association itself. This plan may have resulted in increased work and lengthened reports by referees, to which reports you have had to listen, but it has insured a more careful consideration of

those questions and in some instances, at least, has resulted in greatly improved chapters of methods. The committee desires to take this opportunity to express to the referees and associate referees its appreciation of the splendid assistance given. Because of this plan of handling the revision work the committee has no recommendations to submit for your consideration. This report is one of progress.

The committee held a two days' meeting in the city of Washington on November 16th and 17th, at which time details of the work that could not be handled by correspondence were discussed and determined. At least two new chapters of methods, namely, "Eggs and Egg Products" and "Gelatin", will be introduced in the revised edition and perhaps a third, "Liming Materials", depending upon the action taken at this meeting. Several additional sets of methods, such as methods for the examination of commercial coal tar food dyes, salad dressings, and salt will be added to present chapters. Altogether it is expected that there will be a material increase in the size of the *Book of Methods*.

Probably the most important change editorially is the grouping together in one chapter of all methods for sugars and sugar products. The sugar methods under "Foods and Feeding Stuff" have been combined with those under "Saccharine Products" and placed under the latter chapter, the name of which has been changed to "Sugars and Sugar Products". The chapter title, "Foods and Feeding Stuff—General Methods", has been changed to "Feeding Stuff", and under this will be included the general and special methods for the analysis of feeding stuffs.

Careful consideration has been given to the suggestions received for improving the *Book of Methods*. Curiously enough practically all these suggestions come from users of the book outside the membership of the association. One of the most important of these was the inclusion of a statement in each method showing its limits of accuracy. C. A. Browne discussed briefly the importance of this information in his talk on the opening day of the meeting. The committee considered this suggestion fully but found it impossible to secure the necessary information for methods already adopted. A statement of limits of accuracy is given in a few instances in the present *Book of Methods*, and the number of these will be increased in the revised edition but the proportion of methods giving this information will be small. As a matter of fact, it would be practically impossible to secure such data for all methods at this date. They can best be provided by the referee at the time he makes his recommendations for final action. The matter is referred to here for the reason that the committee believes such information either in the methods themselves or in the report of the proceedings, to which a reference is given, is highly desirable and should be borne in mind by referees in submitting reports for final action.

In this connection consideration was given to the question of the bibliography for the several chapters. It was felt that if a fairly complete bibliography could be provided for each chapter questions such as limits of accuracy, reactions, and basic principles or reasons would be solved through a reference to the publication of the results of collaboration and other studies. This, however, is not possible in the time allotted for the revision now under way. Perhaps it could be handled by a series of monographs on the methods or chapters prepared by members experienced in the different lines. In any event it is a matter that all referees and associate referees should bear in mind in future work. Their reports should always include complete literature references. Another matter that has been forcibly brought to the attention of the committee in the editing of the methods is the failure of authors accurately to describe their methods. It is not to be expected that all authors will write their methods in the same manner, but certainly all methods should be written in such a manner that with a little study the reader can ascertain the apparatus and reagents he is to use and the manipulations he is to perform. For instance, the committee in discussing the form of expression that should be used for the concentrated acids and the dilute acids turned to Chapter I, page 2, Section 5 of the *Book of Methods*, the preparation of solution for the phosphoric acid determination, and found such expressions as these: "dissolve in hydrochloric acid", "boil with 20-30 cc. of strong sulfuric acid", "dissolve in 30 cc. of concentrated nitric and a small quantity of hydrochloric acid", "add 30 cc. of concentrated hydrochloric acid", and "dissolve in 15-30 cc. of strong hydrochloric acid and 3-10 cc. of nitric acid". These expressions for strength of acids are perhaps plain enough for the fertilizer chemist, at least for the method he uses, for he probably never looks into the *Book of Methods* for the details of the determination, but some of those expressions are, to say the least, difficult of interpretation to the analyst who only occasionally has cause to consult the method, and would be to the fertilizer chemist if he found them under the drug methods. Too much care can not be exercised by referees in writing up their methods for publication.

The committee has also given consideration to a number of suggestions received relative to arrangement of methods, cross references, indexing, etc. Several of these will be incorporated in the revised edition. The Committee desires to express its appreciation to the users of the *Book of Methods* who have so kindly responded to the request of a year and two years ago for suggestions and criticisms.

In order that the reports of the proceedings may be complete in regard to the additions and changes made to the methods, there is attached as a part of the report of this committee a list by chapters of the changes made at the 1922 meeting.



## ADDITIONS AND CHANGES TO THE METHODS MADE AT THE 1922 MEETING.

### I. FERTILIZERS.

(1) The Bartlett distillation method<sup>1</sup> for the determination of total boric acid in mixed fertilizers and fertilizer materials adopted as an official method. (First action as an official method.)

(2) The Ross-Deemer method<sup>2</sup> for the determination of water-soluble boric acid in mixed fertilizers and fertilizer materials adopted as an official method. (First action as an official method.)

(3) A method<sup>3</sup> for the preparation of the ammonium citrate solution in the determination of citrate-insoluble phosphoric acid adopted as an official method. (First action as an official method.)

(4) A method<sup>4</sup> for the determination of citrate-insoluble phosphoric acid in precipitated phosphates adopted as an official method. (Final action.)

(5) The Wagner method<sup>5</sup> (gravimetric and volumetric procedures) for the determination of citric acid-soluble phosphoric acid in basic slag adopted as an official method. (Final action.)

### II. INORGANIC PLANT CONSTITUENTS.

(1) The magnesium nitrate method<sup>6</sup> for the determination of sulfur in plant material including the seed of plants adopted as a tentative method.

(2) A method for the determination of phosphorus<sup>7</sup> employing the filtrate from the sulfur determination adopted as a tentative method.

### III. WATERS.

Methods for the determination of copper<sup>8</sup>, lead<sup>9</sup>, and zinc<sup>10</sup> in potable waters adopted as tentative methods.

### IV. TANNING MATERIALS.

No additions or changes made at the 1922 meeting.

### V. LEATHERS.

No additions or changes made at the 1922 meeting.

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 90.

<sup>2</sup> *Ibid.*, 1922, 5: 327.

<sup>3</sup> *Ibid.*, 1923, 6: 390.

<sup>4</sup> *Ibid.*, 289.

<sup>5</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 14.

<sup>6</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 415.

<sup>7</sup> *Ibid.*, 416.

<sup>8</sup> *Ibid.*, 307.

<sup>9</sup> *Ibid.*, 1922, 5: 382.

<sup>10</sup> *Ibid.*, 383.

## VI. INSECTICIDES AND FUNGICIDES.

(1) The mercury-thiocyanate method<sup>1</sup> for the determination of zinc oxide in zinc arsenite adopted as an official method. (Final action.)

(2) Method I<sup>2</sup> for the determination of calcium oxide in calcium arsenate adopted as an official method. (Final action.)

(3) Method II<sup>3</sup> for the determination of calcium oxide in calcium arsenate adopted as an official method. (Final action.)

(4) Under the heading "General Procedure for the Analysis of a Product Containing Arsenic, Lead, etc", a method<sup>4</sup> for the determination of zinc oxide was adopted as an official method. (Final action.)

(5) The hydrazine distillation method<sup>5</sup> for the determination of total arsenic in Paris green adopted as an official method. (First action as an official method.)

## VII. FOODS AND FEEDING STUFFS.

(1) A microscopical method<sup>6</sup> for the determination of rice hulls in rice bran adopted as a tentative method.

(2) A method<sup>7</sup> for the determination of grit in poultry feed and similar feeds adopted as a tentative method.

(3) A method<sup>7</sup> for the determination of bone in meat scraps adopted as a tentative method.

## VIII. SACCHARINE PRODUCTS.

(1) Method III<sup>8</sup> for the determination of ash as sulfated ash dropped. (First action.)

(2) Methods I and II<sup>8</sup> for the determination of ash amended by adding the sentence, "Take up the residue with a little ammonium carbonate solution, re-evaporate, and heat again in the muffle at a very dull heat to constant weight". (First action.)

## IX. FOOD PRESERVATIVES.

No additions or changes made at the 1922 meeting.

## X. COLORING MATTERS IN FOODS.

No additions or changes made at the 1922 meeting.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 392.

<sup>2</sup> *Ibid.*, 395.

<sup>3</sup> *Ibid.*, 396.

<sup>4</sup> *Ibid.*, 398.

<sup>5</sup> *Ibid.*, 402.

<sup>6</sup> *Ibid.*, 1921, 5: 77.

<sup>7</sup> *Ibid.*, 1922, 5: 424.

<sup>8</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 105.

## XI. METALS IN FOODS.

The Gutzeit method<sup>1</sup> for the determination of arsenic modified to permit the use of hydrochloric acid as an alternative acid and the method as modified adopted as official. (First action as an official method.)

## XII. FRUITS AND FRUIT PRODUCTS.

(1) The method<sup>2</sup> for the determination of moisture in all dried fruits adopted as an official method. (Final action.)

(2) The method for the determination of moisture<sup>3</sup> in dried apples continued as a tentative method.

## XIII. CANNED VEGETABLES.

No additions or changes made at the 1922 meeting.

## XIV. CEREAL FOODS.

(1) A method for the determination of fat<sup>4</sup> in baked cereal products adopted as an official method. (First action as an official method.)

(2) A method for the determination of chlorine<sup>5</sup> in bleached flours adopted as a tentative method.

(3) The method for the determination of moisture<sup>6</sup> amplified. (First action.)

(4) The method for the determination of ash<sup>6</sup> amplified. (First action.)

(5) The method for the determination of protein in wheat flour<sup>7</sup> extended to cover the same determination in wheat. (First action.)

## XV. WINES.

No additions or changes made at the 1922 meeting.

## XVI. DISTILLED LIQUORS.

No additions or changes made at the 1922 meeting.

## XVII. BEERS.

No additions or changes made at the 1922 meeting.

## XVIII. VINEGARS.

The method for the physical examination<sup>8</sup> of the sample made official. (Final action as an official method.)

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<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 147.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 273.

<sup>3</sup> *Ibid.*, 274.

<sup>4</sup> *Ibid.*, 1922, 6: 63.

<sup>5</sup> *Ibid.*, 1923, 7: 130.

<sup>6</sup> *Assoc. Official Agr. Chemists, Methods*, 1921, 167; *J. Assoc. Official Agr. Chemists*, 1923, 7: 132.

<sup>7</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 275; 7: 132.

<sup>8</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 191.

### **XIX. FLAVORING EXTRACTS.**

No additions or changes made at the 1922 meeting.

### **XX. MEAT AND MEAT PRODUCTS.**

No additions or changes made at the 1922 meeting.

### **XXI. DAIRY PRODUCTS.**

(1) The cryoscopic method for the examination of milk<sup>1</sup> adopted as official. (Final action as an official method.)

(2) The neutral modification of the Roese-Gottlieb method<sup>2</sup> for the determination of fat in malted milk adopted as a tentative method.

### **XXII. FATS AND OILS.**

(1) The alternative method for the preparation of the Wijs solution<sup>3</sup> adopted at the 1921 meeting was dropped.

(2) A slight correction in the method for standardization of the Hanus iodine solution<sup>4</sup> made.

(3) A modification of the Villavecchia test for sesame oils<sup>5</sup> adopted. (First action as official method.)

(4) The wording of the Baudouin test for sesame oil<sup>6</sup> changed slightly.

### **XXIII. SPICES AND CONDIMENTS.**

The method for the determination of crude fiber in prepared mustard<sup>7</sup> modified and adopted as a tentative method.

### **XXIV. CACAO PRODUCTS.**

(1) A method for determining the critical temperature of dissolution in acetic acid<sup>8</sup> of cacao butter adopted as a tentative method.

(2) The acetone-carbon tetrachloride test for cacao butter adopted as a tentative method<sup>9</sup>.

### **XXV. COFFEES.**

No additions or changes made at the 1922 meeting.

### **XXVI. TEAS.**

(1) The Bailey-Andrew method<sup>10</sup> for the determination of caffeine adopted as official. (Final action.)

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 172, 470, 494; 6: 424.

<sup>2</sup> *Ibid.*, 1923, 6: 435.

<sup>3</sup> *Ibid.*, 440.

<sup>4</sup> *Ibid.*, 444; *Assoc. Official Agr. Chemists, Methods*, 1921, 244.

<sup>5</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 444.

<sup>6</sup> *Ibid.*, 443.

<sup>7</sup> *Ibid.*, 7: 141.

<sup>8</sup> *Ibid.*, 6: 278; 7: 150.

<sup>9</sup> *Ibid.*, 6: 279; 7: 150.

<sup>10</sup> *Ibid.*, 1922, 5: 292.

(2) A method for the determination of water extract<sup>1</sup> adopted as official. (First action.)

## XXVII. BAKING POWDERS AND BAKING CHEMICALS.

A method for the neutralization of mono-calcium phosphate<sup>2</sup> adopted as a tentative method.

## XXVIII. DRUGS.

(1) A method for the preparation of sample of acetylsalicylic acid<sup>3</sup> for the determination of the melting point adopted as a tentative method.

(2) The fuming sulfuric acid method<sup>4</sup> for the examination of turpentine adopted as an official method. (First action as an official method.)

(3) The sulfuric-nitric acid method<sup>5</sup> for the examination of turpentine adopted as a tentative method.

(4) The method for the assay of strychnine in liquids<sup>6</sup>, including both gravimetric and volumetric procedures, adopted as official. (Final action.)

(5) The method for the assay of strychnine in tablets<sup>6</sup>, including both the gravimetric and volumetric procedures, adopted as official. (Final action.)

(6) Methods for the qualitative and quantitative determination of morphine, codeine, and diacetylmorphine<sup>7</sup> adopted as official. (First action as official methods.)

(7) Two methods for the assay of procaine<sup>8</sup> adopted as official. (First action as official methods.)

(8) Qualitative and quantitative methods for the assay of arsphenamine and neoarsphenamine<sup>9</sup> adopted as official. (First action as official methods.)

(9) A modified method for the determination of arsenic in arsphenamine and neoarsphenamine<sup>10</sup> adopted as a tentative method.

(10) The iodine method for the assay of methylene blue<sup>11</sup> adopted as a tentative method.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 280.

<sup>2</sup> *Ibid.*, 448.

<sup>3</sup> *Ibid.*, 1922, 5: 582.

<sup>4</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 466.

<sup>5</sup> *Ibid.*, 1922, 5: 552.

<sup>6</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 301; *J. Assoc. Official Agr. Chemists* 1922, 5: 564.

<sup>7</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 150.

<sup>8</sup> *Ibid.*, 1922, 5: 590.

<sup>9</sup> *Ibid.*, 1923, 6: 461.

<sup>10</sup> *Ibid.*, 463.

<sup>11</sup> *Ibid.*, 7: 20.

**XXIX. SOILS.**

No additions or changes made at the 1922 meeting.

**XXX. REFERENCE TABLES.**

No additions or changes made at the 1922 meeting.

R. E. DOOLITTLE,	J. W. SALE,
B. B. ROSS,	G. W. HOOVER,
A. J. PATTEN,	W. H. MACINTIRE.

*Committee on Editing Methods of Analysis.*

Adopted.

## REPORT OF THE BOARD OF EDITORS.

By R. W. BALCOM (Bureau of Chemistry, Washington, D. C.),  
Chairman.

The association last year voted<sup>1</sup> approval of the plan of the American Public Health Association for a joint publication of the bacteriological and chemical methods for the examination of milk, on condition that the identity of the chemical methods as the A. O. A. C. methods be retained, and authorized the Board of Editors to attend to the details of such a publication.

The matter of the revision of the association's methods for the chemical examination of milk to include any changes that had been made since the 1920 edition of "Methods of Analysis" was published, and of making such other rearrangement of the text as was found to be necessary to eliminate the cross-references used in the chapter on Dairy Products in "Methods of Analysis" was attended to by the Committee on Editing Methods of Analysis, with the assistance of Julius Hortvet, Referee on Dairy Products. The form of publication finally agreed upon is shown in the pamphlet, "Standard Methods of Milk Analysis of the American Public Health Association and the Association of Official Agricultural Chemists", which came from the press early this year. It was arranged that the American Public Health Association should bear the expense of the publication of this pamphlet, and that this association should receive 100 copies free of charge. Some of these 100 copies have already been distributed gratis to members of the association who were known to be particularly interested in the methods for the examination of milk. Any member of the association who desires a copy may obtain one from the Chairman of the Board as long as the supply lasts. The American Public Health Association, through its secretary, has expressed its appreciation of the cooperation of this association in preparing this joint publication.

Last year it was the duty of the Board of Editors to direct attention to the very serious condition of *The Journal's* finances, and an appeal was made for the earnest support of every member of the association. Active assistance in increasing the number of subscriptions to *The Journal* was requested, and the Board pledged itself to do everything possible to reduce expenses. The Board later directed a letter to many of the members of the association, giving a list of subscribers in their respective States and asking for names and addresses of any others that might be interested. The response was very gratifying. A circular letter descriptive of *The Journal* was then sent to each prospect, with the result that some new subscriptions were obtained, but these

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 240.

new subscriptions and those obtained throughout the year in other ways have no more than offset the number of cancellations, so that the number of subscriptions on the books at the present time is no greater than that reported last year. Nevertheless, the Board is able to report that there has been a great improvement in the finances. A marked reduction in charges for printing, as well as better service, has been obtained from the printer. In addition to this, the management of the advertising material was taken over by the Chairman of the Board. This resulted in some increase in the number of advertisements and also in a saving to the association of the 20 per cent formerly paid to an advertising agent. As a result of these and other measures, the net cost of the printing of *The Journal* has been reduced by approximately \$2,000, and it is now nearly covered by the returns from subscriptions.

The sale of "Methods of Analysis" has continued uninterruptedly. A year ago 600 copies remained unsold, all of which had been paid for. These, with the exception of about 30 copies, have been sold, and the remainder will probably be disposed of by the end of the calendar year. The proceeds from these sales have gone far toward wiping out the deficit that has confronted the association for a long time, and it is now possible to meet the printer's bills within a reasonable period of time after they are presented. Funds with which to meet the bill of August 31st for No. 1 of Volume VII, for example, will be in hand by the end of the present month. While this is very encouraging, it is necessary to emphasize that *The Journal* needs the continued support of the individual members of the association.

This support can be manifested not only by efforts to increase the number of subscriptions, but also by the contribution of any articles suitable for publication in *The Journal*. The Board has been disappointed that so few of these have been received during the past year. Those accepted have been printed with as much dispatch as the limitations of a quarterly publication permit.

The printing of the committee reports and recommendations in the first number of *The Journal* after the annual meeting, a policy adopted by the Board last year, has apparently met with universal approval. It is believed that this policy and also that of carrying contributed articles in each number should be continued, but for the success of this second policy and also for the greatest success of *The Journal* itself, it is necessary that a regular supply of high-grade papers be submitted for publication from as many different sources as possible. Members of the association are urged to bear this in mind.

A financial statement that shows receipts and disbursements by the Board during the association year is appended.



## FINANCIAL REPORT ON PUBLICATIONS FROM

By R. W. BALCOM (Bureau of Chemistry, Wash-

## RECEIPTS.

1922			
Oct. 31	Bank balance.....		\$ 332.56
	Total deposits.....	\$8,879.27	
	Less redeposited checks.....	\$14.00	
	Less 2 checks for collection.....	9.40	
		<hr/>	
		23.40	
			8,855.87
			<hr/>
			\$9,188.45

## DETAILED STATEMENTS RELATIVE TO RECEIPTS.

*Journal subscriptions.*

No. Ordered	Price Each	Total Cost
67	\$5.50	\$ 368.50
720	5.00	3,600.00
93	4.40	409.20
1	4.20	4.20
314	4.00	1,256.00
7	3.75	26.25
3	3.36	10.08
4	3.00	12.00
2	2.80	5.60
2	2.50	5.00
2	2.00	4.00
3	1.75	5.25
48	1.50	72.00
4	1.40	5.60
7	1.25	8.75
14	1.00	14.00
		<hr/>
Total.....		\$5,806.43
Plus gain on exchange.....		4.91
		<hr/>
Total.....		\$5,811.34

NOVEMBER 1, 1922 TO NOVEMBER 1, 1923.

ington D. C.), *Chairman, Board of Editors.*

### DISBURSEMENTS.

1922		Amount	Check No.
Nov. 1	J. W. Sample, reimbursement on overpayment <i>Journal</i> subscription.....	\$ 2.00	1
Nov. 3	Farran's Transfer and Storage .....	5.44	2
Nov. 27	University of Saskatchewan, reimbursement on overpayment of <i>Journal</i> subscription .....	.50	3
Nov. 28	Janet K. Smith, office expenses .....	25.00	4
Dec. 1	Industrial Printing Co., on account .....	500.00	5
Dec. 1	J. M. Hanson-Bennett, reimbursement on overpayment of <i>Journal</i> subscription.....	.50	6
Dec. 16	Wm. E. Shaefer, reimbursement on overpayment of <i>Journal</i> subscription .....	1.00	7
Dec. 21	Postmaster, Washington, D. C., box rent quarter ending March 31, 1923.....	2.00	8
Dec. 22	Industrial Printing Co., bill 11-15-22 .....	28.75	9
Dec. 22	Industrial Printing Co., balance payment on bill 5-21-22 .....	579.35	10
1923			
Jan. 6	Postmaster, Washington, D. C., 5000 special request window envelopes .....	119.30	11
Jan. 6	Industrial Printing Co., on account .....	500.00	12
Jan. 6	Farran's Transfer and Storage .....	2.29	13
Jan. 6	Marian E. Lapp, reimbursement on trip to Baltimore .....	4.23	14
Jan. 6	Sears, Roebuck & Co., for back numbers of <i>Journal</i> .....	7.00	15
Jan. 13	Janet K. Smith, office expenses .....	25.00	16
Jan. 20	Industrial Printing Co., on account .....	500.00	17
Jan. 25	Farran's Transfer and Storage .....	21.25	18
Feb. -1	Moore-Cottrell, reimbursement on overpayment on subscription to <i>Journal</i> .....	.40	19
Feb. 1	Wm. Dawson & Son, reimbursement on overpayment on subscription to <i>Journal</i> .....	2.50	20
Feb. 3	Industrial Printing Co., on account .....	500.00	21
Feb. 17	Industrial Printing Co., balance payment on bill 7-25-22 .....	537.45	22
Feb. 23	Janet K. Smith, office expenses .....	25.00	23
Feb. 26	Waldo P. Stanford, reimbursement on overpayment on <i>Book of Methods</i> .....	1.00	24
Mar. 9	Janet K. Smith, office expenses .....	25.00	26
Mar. 14	Industrial Printing Co., on account .....	400.00	27
Mar. 14	Farran's Transfer and Storage .....	2.61	28
April 2	Williams & Wilkins, 6 copies of Vol. III, No. 1 @ \$1.00 .....	6.00	29
April 2	Postmaster, Washington, D. C., box rent for quarter ending June 30, 1923 .....	2.00	30
April 2	Industrial Printing Co., on account .....	400.00	31
April 2	W. G. Haywood, Vols. I, II and III @ \$4.00.....	12.00	32
April 6	W. S. Hubbard, Vols. I and II @ \$4.00.....	8.00	33
April 6	W. C. Leigh, Vol. II @ \$5.00 .....	5.00	34
April 14	J. Edw. Porter, old numbers of <i>Journal</i> .....	3.13	35
April 14	New England Confectionery Co., Vols. I and II .....	10.00	36
April 21	Janet K. Smith, office expenses .....	25.00	37
April 28	Industrial Printing Co., balance payment on bill 11-29-22 .....	429.28	38
May 5	American Agricultural Chemical Co., bill No. O-1315.....	8.75	39
May 5	C. B. Gnadinger, back numbers of <i>Journal</i> .....	6.88	40
May 23	Janet K. Smith, office expenses .....	25.00	41
June 2	Industrial Printing Co., on account.....	400.00	42
June 8	Farran's Transfer and Storage .....	4.73	43
June 14	Milton Hersey Co., reimbursement on overpayment on <i>Journal</i> subscription.....	.50	44
June 21	Postmaster, Washington, D. C., box rent for quarter ending September 30, 1923 .....	2.00	45

## RECEIPTS—Continued.

*Methods subscriptions.*

No. Ordered	Price Each	Total Cost
21	\$5.50	\$ 115.50
343	5.00	1,715.00
26	4.40	114.40
113	4.00	452.00
Total.....		\$2,396.90
Plus gain on exchange		3.57
Total...		\$2,400.47

*Advertisements.*

No. Ordered	Price Each	Total Cost
9	\$25.00	\$225.00
7	15.00	105.00
Collected on old accounts.....		297.30
Total. . . . .		\$627.30

*Reprints.*

University of Tennessee.....	6.76
Total, <i>Journal, Methods</i> , Advertisements and Reprints	\$8,845.87
Plus checks returned because of excess payment . . .	10.00
Plus bank balance . . . . .	332.58
	<u>\$9,188.45</u>

Approved.

## FINANCIAL REPORT OF THE SECRETARY-TREASURER

By W. W. SKINNER (Bureau of

## RECEIPTS.

1922		
Nov. 1	Bank balance.....	\$ 216.87
Nov. 29	Dues from 2 State institutions received too late for inclusion in 1922 report	\$ 10.00
	Dues for 1923 from 1 State institution	5.00
		15.00
1923		
Mar. 10	Dues from 1 State institution received too late for inclusion in 1922 report.....	\$ 5.00
	Dues for 1923 from 5 Canadian and State institutions . . .	25.00
		30.00
May 5	Dues for 1923 from 6 State institutions . . . . .	30.00
May 12	Dues for 1923 from 10 Canadian and State institutions . . .	50.00
May 19	Dues for 1923 from 4 Canadian and State institutions . . .	20.00
May 26	Dues for 1923 from 4 Canadian and State institutions . . .	20.00
June 2	Dues for 1923 from 4 State institutions . . . . .	20.00
June 9	Dues for 1923 from 5 State institutions . . . . .	25.00
July 7	Dues for 1923 from 7 State institutions . . . . .	35.00
July 14	Dues for 1923 from 2 State institutions . . . . .	10.00
July 18	Dues for 1923 from 2 State institutions . . . . .	10.00
Oct. 21	Dues for 1923 from 11 State institutions . . . . .	55.00
	Total receipts . . . . .	\$ 536.87

DISBURSEMENTS—*Continued.*

		Amount	Check No.
June 25	Industrial Printing Co., balance payment on bill of 11-29-22..	540.33	46
July 3	Industrial Printing Co., bill 2-28-23.....	40.85	47
July 3	F. W. Faxon Co., reimbursement on subscription.....	4.00	48
July 7	Janet K. Smith, office expenses.....	35.00	49
July 10	G. S. Fraps, reimbursement on overpayment on subscription to <i>Journal</i> .....	1.00	50
July 16	M. R. Weir, reimbursement on overpayment on <i>Journal</i> sub- scription.....	1.00	51
July 31	Industrial Printing Co., on account.....	500.00	53
Aug. 16	U. S. Flour Mills Co., reimbursement on <i>Book of Methods</i> ...	5.00	54
Aug. 16	Edw. J. Wheeler, back numbers of <i>Journal</i> .....	10.00	55
Aug. 21	Postmaster, Washington, D. C., for mailing <i>Journals</i> .....	15.00	56
Aug. 28	Farran's Transfer and Storage.....	3.59	57
Aug. 28	Janet K. Smith, office expenses.....	25.00	58
Aug. 31	Globe Grain and Milling Co., refund on <i>Book of Methods</i> ...	.50	59
Sept. 4	Industrial Printing Co., on account.....	500.00	60
Sept. 4	J. T. Keister, back numbers of <i>Journal</i> .....	2.00	61
Sept. 10	Industrial Printing Co., balance bill of 3-27-23.....	324.45	62
Sept. 10	Industrial Printing Co., bills 5-22-23 and 6-6-23.....	35.51	63
Sept. 21	Postmaster, Washington, D. C., box rent for quarter ending December 31, 1923.....	2.00	64
Sept. 22	John Wiley & Sons, for book.....	1.60	65
Sept. 22	Industrial Printing Co., on account.....	500.00	66
Oct. 6	Industrial Printing Co., on account.....	500.00	67
Oct. 15	Moore-Cottrell, reimbursement on subscription to <i>Journal</i> ...	4.00	68
Oct. 17	Industrial Printing Co., balance bill of 6-20-23.....	365.05	69
Oct. 31	Bank balance.....	606.73	
		<u>\$9,188.45</u>	

NOTE:—Checks numbered 25 and 52 cancelled.

FROM NOVEMBER 1, 1922 TO NOVEMBER 1, 1923.  
Chemistry, Washington, D. C.).

## DISBURSEMENTS.

		Amount	Check No.
1922			
Nov. 27	Marian E. Lapp, reimbursement for expenses 1922 meeting..	\$27.00	25
Dec. 4	H. C. Hunter, for lettering badges for 1922 meeting.....	6.00	26
1923			
Feb. 1	R. P. Andrews, 10,000 sheets paper.....	12.85	27
Sept. 18	Cash for postage for mailing announcements of 1923 meeting	25.00	28
Sept. 22	Industrial Printing Co., for 1500 programs of 1923 meeting..	32.00	29
Oct. 4	Bastian Bros., for 300 hadges for 1923 meeting.....	19.48	30
Oct. 31	Bank balance.....	414.54	

Total.....\$ 536.87

No report was made by the Committee on Quartz Plate Standardization and Normal Weight.

## REPORT OF THE COMMITTEE ON DEFINITIONS OF TERMS AND INTERPRETATION OF RESULTS ON FERTILIZERS.

An open meeting of the Committee on Definitions of Terms and Interpretation of Results on Fertilizers was held, J. W. Kellogg acting as chairman. The following report, submitted by H. D. Haskins, chairman of the committee, was read by L. S. Walker.

### INFERIOR FORMS OF ORGANIC NITROGEN.

For the past eighteen years or more the quality of the organic nitrogen in mixed fertilizers has been studied by the agricultural chemist. For the past thirteen years the Massachusetts Agricultural Experiment Station has, in the tabulation of the analytical data on fertilizer inspection, indicated the quality of the water-insoluble organic nitrogen on all brands analyzed. That this has been responsible for the improvement in the quality of the organic nitrogen that the fertilizers have contained there can be no question. The two laboratory methods more commonly used in studying the activity of the water-insoluble nitrogen in fertilizers are known as the "Jones Alkaline Permanganate Method" and the "Street Neutral Permanganate Method". No one having a correct understanding of the matter disputes the chemist's ability by means of these methods to pick out those brands that contain the more inferior forms of water-insoluble organic nitrogen. There does exist, however, considerable difference of opinion as to what the results show and how they shall be interpreted.

Nitrogen activity by the laboratory methods does not mean the same thing as nitrogen availability by vegetation tests. In fact, a comparison made on many samples both at the Rhode Island Agricultural Experiment Station and the Massachusetts Station shows that the neutral permanganate method gives much higher figures in activities than does the vegetation test in availabilities. On the other hand, the alkaline permanganate method not infrequently, particularly in case of mixtures containing organic vegetable ammoniates, gives considerably lower figures in activity than does the vegetation test in availability. It is generally understood by the trade and by the control chemist that any fertilizer containing its water-insoluble nitrogen in forms to give an activity of less than 80 by the neutral and less than 50 by the alkaline permanganate method shall be considered as containing organic nitrogen of an inferior form. As a matter of record it may be said that a belief

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<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 11.

exists in the minds of some chemists who have given the matter careful thought and study that it would not be an injustice to the manufacturer to increase the passing mark in case of the alkaline method by five points, making it 55 instead of 50. It is not uncommon for two chemists in studying the organic nitrogen activity on the same sample of fertilizer to obtain results which vary from one to three points, and in some cases even more; particularly is this apt to be the case if the type of apparatus used in the two laboratories is different. It might also be said that in this, as in almost all operations, experience is an important factor.

In the 1922 fertilizer inspection of the State of Massachusetts two brands of fertilizer representing grades 2-8-2 and 2-8-3 were found by the laboratory methods to contain organic nitrogen of an inferior quality. At the request of the manufacturer the sealed duplicate samples, as provided by the law, were forwarded for checking purposes to their chemist, who reported back a test of over 50 activity on one of the brands; the check results were, however, under 55 activity in all cases. A study at the Massachusetts Agricultural Experiment Station of the results of analysis of grades 2-8-2 and 2-8-3 put out by the manufacturer showed that 14 brands and 48 samples of the 2-8-2 grade and 16 brands and 48 samples of the 2-8-3 grade had given activities of water-insoluble organic nitrogen between 46 and 54 by the alkaline permanganate method. It seemed, therefore, that this was a good opportunity to secure data by the use of vegetation tests as to the actual crop-producing power of the water-insoluble nitrogen in these two types of fertilizer that had shown an average activity of over 50 and under 55 by the alkaline method, in order to confirm the reliability of the laboratory method in detecting the presence of low-grade organic ammoniates. Plans were made, therefore, to conduct such tests not only with the two brands in question, but also with the various brands belonging to the same two grades that were put out by this company.

#### VEGETATION TESTS FOR NITROGEN ACTIVITY.

The soil used for the experiment was taken from one of the Massachusetts Experiment Station fields. No nitrogen fertilizer or animal manure has been applied to this soil since 1890. It has received annually during this period, per acre basis, 320 pounds of acidulated phosphate and 160 pounds of muriate of potash. The only nitrogen that the soil has received for nearly a third of a century has resulted from crop residues or natural sources common to fields under usual farm management.

One part by weight of this soil was mixed with two parts of sifted sand, and 43 pounds of this mixture was weighed into each pot.

Three pots were used for each experiment, and each pot received the following basic fertilizer application:

25 grams of fine ground limestone,  
5 grams of sulfate of potash-magnesia,  
5 grams of muriate of potash,  
9 grams of acid phosphate, and  
18 grams of basic slag phosphate.

*Nitrogen applications.*

SOURCE OF NITROGEN	grams per pot
None.....	..
Nitrate of soda.....	0.42
Dried red blood.....	0.42*
Dried red blood.....	0.84*
Washed dried red blood.....	0.42
Washed dried red blood.....	0.84
Washed fertilizer, grade 2-8-2.	0.42
Washed fertilizer, grade 2-8-2.	0.84
Washed fertilizer, grade 2-8-3.	0.42
Washed fertilizer, grade 2-8-3.	0.84

\*0.42 grams per pot equivalent to 59.5 pounds of nitrogen per acre.  
0.84 grams equivalent to 119 pounds per acre.

In case of the commercial fertilizers and one series of the dried blood, these were washed with successive portions of distilled water so as to remove all water-soluble nitrogen. The water-insoluble portion, dried at a low temperature, was used in the vegetation pot work after being tested for its nitrogen. Each fertilizer residue was also tested for its nitrogen activity by both the alkaline and neutral permanganate methods in order to secure data for comparison with the vegetation experiment.

The various nitrogen products, as well as the basic fertilizer applications, were mixed with the whole volume of soil in each pot.

Oats were selected as the crop to be grown and were thinned to ten plants per pot. The crop was harvested when in milk by cutting even with the ground, each pot having its full quota of plants at harvest time. Dry matter determinations were made on the air dried products. The care of the experiment during the growing season was in charge of R. L. Coffin, who has had many years of experience in this line of work.

The following table gives the yield per individual pot, figured on a dry-matter basis. It also gives the average dry-matter yield per pot; the average increase in dry matter over the no-nitrogen pots, due to the nitrogen source used; the relative nitrogen availability calculated from the average increased yields over the no-nitrogen pots, the average increase yields from the washed dried blood being placed at 80; and for the sake of comparison, the average activity of the nitrogen from each source of organic nitrogen used, as determined chemically by the two laboratory methods. In case of the unwashed blood these activi-

ties are calculated on the total nitrogen basis and would include the water-soluble as well as the active-insoluble nitrogen present.

POT NUMBER	SOURCE OF NITROGEN	WATER-INSOLUBLE NITROGEN PER POT <sup>2</sup>	YIELD OF DRY MATTER PER POT	AVERAGE YIELD OF DRY MATTER PER POT	AVERAGE INCREASE IN DRY MATTER OVER NO- NITROGEN POTS	RELATIVE NITROGEN AVAILABILITY WASHED DRY BLOOD AT 80. BASIS DRY MATTER RECOVERED	COMPARATIVE NITROGEN ACTIVITY BY ALKALINE PER- MANGANATE METHOD	COMPARATIVE NITROGEN ACTIVITY BY NEUTRAL PER- MANGANATE METHOD
		grams	grams	grams	grams			
1 A	None . . . . .		14.68					
1 B	None . . . . .		16.03	14.93	..	..	..	..
1 C	None . . . . .		14.07					
2 A	Nitrate of soda . . . . .	0.42	20.31					
2 B	Nitrate of soda . . . . .	0.42	21.36	20.84	5.91	40.94	..	..
2 C	Nitrate of soda . . . . .	0.42	20.85					
3 A	Dried blood, unwashed .	0.42	24.90					
3 B	Dried blood, unwashed .	0.42	24.93	25.62	10.69	74.04	78.82	93.80
3 C	Dried blood, unwashed .	0.42	27.04					
4 A	Dried blood, unwashed .	0.84	30.96					
4 B	Dried blood, unwashed .	0.84	31.60	31.72	16.79	73.92	78.82	93.80
4 C	Dried blood, unwashed .	0.84	32.61					
5 A	Fertilizer 2-8-2 washed†	0.42	17.77					
5 B	Fertilizer 2-8-2 washed	0.42	21.28	18.80	3.87	26.81	44.64	73.80
5 C	Fertilizer 2-8-2 washed	0.42	17.35					
6 A	Fertilizer 2-8-2 washed	0.84	21.53					
6 B	Fertilizer 2-8-2 washed	0.84	20.16	21.06	6.13	26.99	44.64	73.80
6 C	Fertilizer 2-8-2 washed	0.84	21.50					
7 A	Fertilizer 2-8-3 washed‡	0.42	17.95					
7 B	Fertilizer 2-8-3 washed .	0.42	17.72	17.43	2.50	17.32	47.60	77.60
7 C	Fertilizer 2-8-3 washed	0.42	16.61					
8 A	Fertilizer 2-8-3 washed	0.84	20.21					
8 B	Fertilizer 2-8-3 washed	0.84	21.82	20.32	5.39	23.73	47.60	77.60
8 C	Fertilizer 2-8-3 washed	0.84	18.94					
9 A	Dried blood washed . . .	0.42	29.02					
9 B	Dried blood washed . . .	0.42	24.08	26.48	11.55	80.00	75.40	91.40
9 C	Dried blood washed . . .	0.42	26.35					
10 A	Dried blood washed . . .	0.84	30.15					
10 B	Dried blood washed . . .	0.84	34.70	33.10	18.17	80.00	75.40	91.40
10 C	Dried blood washed . . .	0.84	34.44					

\*Dried blood 3 A to 4 C, inclusive, received their nitrogen from unwashed material.

†Composites made by equal weights of 14 brands and 48 samples.

‡Composites made by equal weights of 16 brands and 48 samples.

NOTE.—The insoluble nitrogen activities, as taken from the 1922 inspection data on the above-mentioned two grades of mixed fertilizer, as determined by the alkaline permanganate method, varied from 46 to 54 per cent. The activities given in the table were made on the washed and dried residues prepared for this vegetation test.



A study of the table suggests the following conclusions:

1. Both grades of fertilizer which, upon individual analysis of the thirty brands of which the two grades were composed, showed water-insoluble nitrogen activities ranging from 46 to 54 per cent, actually showed in average nitrogen availability as measured by their crop-producing power less than 24 per cent, the 2-8-2 averaging 26.90 and the 2-8-3, 20.53.

2. That on these thirty particular brands it apparently would have worked no injustice upon the manufacturer had the passing mark or standard been set at 55 instead of 50 for the alkaline permanganate method. Had the standard been 55 the water-insoluble nitrogen in each case would have been graded "inferior", a fact that is certainly borne out in this experiment by the actual crop-producing power of the different brands as compared with dried blood.

3. The neutral permanganate method was quite as effective as the alkaline method in grading the nitrogen supplied by the blood and the two grades of mixed fertilizer, although the latter method gave insoluble nitrogen activities that more nearly correspond to the availabilities as established by the vegetation test.

4. Judging from this experiment, there would be ample justification in raising the standard of the alkaline method to 55.

A lengthy discussion of the different State fertilizer laws, Haskins' report, and of numerous definitions, including those for basic phosphate slag, the word "lime" as applied to fertilizers, and the interpretation of results on organic nitrogen in mixed fertilizers, followed.

Much interest was shown, and general satisfaction was expressed that such an opportunity was afforded for the exchange of ideas relating to fertilizer problems.

The committee recommended the following for tentative interpretations and definitions of terms:

#### 1. BASIC PHOSPHATE SLAG.

*Basic phosphate slag* is a by-product in the manufacture of steel from phosphatic iron ores. The product shall be finely ground and shall contain no admixture of materials other than what results in the original process of manufacture. It shall contain not less than twelve per cent (12%) of total phosphoric acid ( $P_2O_5$ ), not less than eighty per cent (80%) of which shall be soluble in two per cent (2%) citric acid solution according to the Wagner method of analysis. Any other phosphate slag not conforming to this definition shall be designated *low grade*.

#### 2. INTERPRETATION OF THE WORD "LIME" AS APPLIED TO FERTILIZERS.

The term *lime* shall not be used in the registration, labelling, or guaranteeing of fertilizers or fertilizing materials, unless the lime is in a form to neutralize soil acidity, such as the oxide, hydroxide, or carbonate, or equivalent magnesia compounds.

## 3. DRIED PULVERIZED OR SHREDDED MANURES.

*Dried pulverized or shredded manure* shall be only what the name indicates, and not mixtures of manures and other materials.

## 4. MANURE SALTS.

*Manure salts* shall be understood to mean potash salts containing high percentages of chloride and from twenty per cent (20%) to thirty per cent (30%) of potash ( $K_2O$ ). The term *double manure salts* should be discontinued.

## 5. SULFATE OF POTASH-MAGNESIA.

*Sulfate of potash-magnesia* is a potash salt containing not less than twenty-five per cent (25%) of potash ( $K_2O$ ), not less than twenty-five per cent (25%) of sulfate of magnesia, and not more than two and five-tenths per cent (2.5%) of chlorine.

6. INTERPRETATION OF RESULTS ON ORGANIC NITROGEN  
IN MIXED FERTILIZERS.

The results of the determinations of organic nitrogen in mixed fertilizers obtained by the neutral or alkaline permanganate method shall be interpreted as follows:

(a) The methods shall be used only on mixed fertilizers containing water-insoluble nitrogen amounting to one-third ( $\frac{1}{3}$ ) or more of the total nitrogen found. The nitrogen shall be passed as satisfactory in mixed fertilizers if more than two-thirds ( $\frac{2}{3}$ ) of the total nitrogen guaranteed is water-soluble.

(b) The water-insoluble nitrogen in mixed fertilizers showing an activity of fifty per cent (50%) or more by the alkaline permanganate method or seventy-five per cent (75%) or more by the neutral permanganate method shall be classed as *satisfactory*. The nitrogen showing activities below these figures shall be classed as *inferior*.

The following subjects are herewith submitted for consideration and study:

The meanings of the terms *formula*, *grade*, *analysis* when used as *high analysis*, etc. Definitions for the words *brand* and *unit*.

Definitions for the following subjects were not acted upon and were continued for consideration next year:

Unleached wood ashes,  
Ashes from leached wood,  
Leached wood ashes,  
Dissolved bone and potash.

H. D. HASKINS,      E. G. PROULX,  
R. N. BRACKETT,    J. W. KELLOGG.  
G. S. FRAPS,

*Committee on Definitions of Terms  
and Interpretation of Results on  
Fertilizers.*

Approved.

## FINAL REPORT OF THE SPECIAL COMMITTEE OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEM- ISTS ON THE AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG PHOSPHATES<sup>1</sup>.

At the twenty-eighth annual convention of the Association of Official Agricultural Chemists in 1911, a special committee was appointed to outline and make provisions for conducting vegetation experiments, both in pots and in the field, in order to accumulate data as to the availability of the phosphoric acid contained in Thomas-Bessemer basic phosphatic slag. The ultimate object of the investigation was to determine the reliability of the Wagner method<sup>2</sup> (which was then in use in most foreign countries, and had been tentatively adopted by many control officials in this country)<sup>3</sup> for measuring the availability of the phosphoric acid in basic slag that was being imported and used in some of the States in relatively large quantities.

It was recommended by the Referee on Phosphoric Acid and by Committee A on Recommendations that the Wagner method be adopted provisionally, pending further study and the gathering of more complete data in regard to field and pot experiments. This recommendation was adopted by the association.

In the proceedings of the twenty-ninth annual convention of the association, pages 50-51, will be found the first report of the Basic Slag Committee, which included an outline of the plan for conducting the field vegetation tests.

At the thirtieth annual convention of the association, the committee made a report of progress and presented detailed directions for conducting the pot vegetation work. The chemical composition of the phosphates to be used was also made a part of that report<sup>4</sup>. Subsequent reports of progress have been made to the association from time to time and form a part of the proceedings as published in *The Journal*. Although normally these reports might, and possibly should be made a part of the final report of the committee, for the sake of brevity, and in conformity with a vote of the association taken in 1921, "that the final abbreviated report of the committee be printed in the association *Journal* as soon as ready and space for the same is found available", it would seem that these brief references must suffice.

The final report of the committee consists largely in the brief presenta-

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 254. Received September 18, 1923.

<sup>2</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 14.

<sup>3</sup> Apparently some control officials in this country, in 1908 and earlier, in the inspection of basic slag phosphate were relying upon a test for total phosphoric acid and fineness of the product in estimating its commercial value. In 1907, the Referee on Phosphoric Acid recommended to the association that the fineness of basic slag phosphate be determined according to the plan followed with bone meal, and the commercial value estimated on the basis of total phosphoric acid and fineness of product.

<sup>4</sup> *J. Assoc. Official Agr. Chemists*, 1915, 1: 102.

tion of results of the various investigators, together with additional calculations to show in the final summary tables the general standing of the several brands or grades of phosphatic slag, as compared particularly with superphosphate or acid phosphate, though other sources of phosphoric acid, both in soluble and insoluble form, are included in order to tell the whole story. Although some of the results of the collaborators have been published in bulletin form by the experiment stations that furnished means for doing the work (Hawaii, New Jersey, and Rhode Island), most of the results have been reserved for publication in this final report. It has seemed best, therefore, to report in detail, but in tabular form, the various yields secured. There are indications that in some instances the soils were not sufficiently depleted in phosphoric acid to give clear-cut and positive results. Particularly is this true of the field experiments that were run in Massachusetts and Pennsylvania. The same criticism applies to the following pot experiments: two out of the five series from Massachusetts; two series from New York, Cornell; and six out of nineteen experiments from Texas. While the results of all of these experiments appear under their respective heads, they do not form a part of the summary tables that show the general standing of the different phosphates. With these exceptions, the soils used in the pot work gave results that indicate that they were happily selected and well adapted to the work.

The institutions that took part in this cooperative work and made reports to the committee are located as follows: Hawaii, Illinois, Massachusetts, New Jersey, New York, North Carolina, North Dakota, Pennsylvania, Rhode Island, and Texas. The contributions from these various sources are presented alphabetically.

#### HAWAII EXPERIMENT STATION.

##### POT EXPERIMENTS.

Character of soil: heavy, ferruginous clay, or laterite. Depth of soil: no line of demarcation between soil and subsoil. The soil used was taken to a depth of eight inches, and upon chemical analysis showed the presence of 0.28 per cent of phosphoric acid, 0.33 per cent nitrogen, 0.34 per cent potash, 0.18 per cent lime, 0.34 per cent magnesia, and 12.19 per cent organic matter. Mechanical analysis showed 36.28 per cent clay, 34.54 per cent fine silt, 8.85 per cent silt, 3.68 per cent fine sand, 0.77 per cent coarse sand, and 13.14 per cent organic matter. Lime absorption, Veitch method: 0.236 per cent calcium carbonate. Soil finer than 3 mm., 100 per cent.

Kind and dimensions of pots: tin cans, height 7 inches, diameter 6 inches. Depth of soil in pot, 6 inches. Weight of air-dried soil in pots, 6 pounds.

*Experiment I.*—In the first experiment five crops were grown. Fertilizer applications were made according to the schedule of the Basic

Slag Committee, preceding the growing of the first crop, which was Japanese millet, planted July 31 and harvested October 20, 1913. The soil was then dried out, aerated, returned to the pots, and planted to cowpeas on November 17. This crop was cut on January 17, the product from each pot being weighed separately and returned to the respective pots. Without any further addition of fertilizer the pots were planted to buckwheat on February 6; this crop was harvested March 27. The soil was again dried out, well aerated, and planted to millet on May 18, without further addition of fertilizer. This crop was harvested on August 10. The soil was again dried out, aerated and well mixed, and after a full application of nitrogen and potash, but no phosphoric acid, was again planted to millet.

Supplements to suggested method: plants were watered daily; poor germination in several instances necessitated replanting. The number of plants to be grown in each pot is indicated in Table 1, but an incomplete stand was secured in some cases, as shown.

*Experiment II.*—Another series of experiments was made with the same type of soil, using millet as a crop. Fertilizers were added in the same amounts as in the previous series, with the exception that a complete fertilizer was added before planting the third crop. Cultural treatment was the same as in Experiment I. The results are shown in Table 2.

#### ILLINOIS AGRICULTURAL EXPERIMENT STATION, URBANA.

Pot experiments were begun in 1915 and carried through 1916 and 1917. The tables indicate the crops grown each year. The soil used was a light phase of brown sandy loam containing 1,832 pounds of  $P_2O_5$  per acre in  $6\frac{2}{3}$  inches of the surface soil. The depth of the soil in the field was about 10 inches. Four-gallon glazed earthenware pots,  $10\frac{1}{2}$  inches in diameter, were filled with 6 inches of surface soil underlaid with 4 inches of subsoil, the weight of the surface soil in each pot being 10 kilograms. In 1915, 19.4 grams of finely ground carbonate of lime were added to the surface soil of each pot.

The dates of planting varied from year to year. In 1915, red clover was planted May 24, 10 plants per pot; wheat, May 25, 15 plants per pot; soy beans, May 26, 10 plants per pot; and rape, May 26, 5 plants per pot. The time of harvesting varied, but the crops were matured to produce seed. The crops were dried in light canvas bags suspended in the greenhouse. No chemical analysis was made of the crops. Results are reported on air-dried basis.

Phosphorus in the stated amount and form was added in 1915 and 1916. In 1917, phosphorus was added in the full amount recommended by the committee. Commercial nitrogen and potash were not used in these experiments. The legume crops were used as a manure after the

TABLE I.

## Hawaii Experiment Station. Experiment I.

(Comprising five crops grown on the same soil with only one application of phosphoric acid, which was used on the first crop of millet.)

NUMBER OF POTS EMPLOYED	FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	AFTER FALLOW						AFTER LEGUME					
			Millet I	Cowpeas	Buck- wheat	Millet II	Millet III	Millet I	Cow- peas	Buck- wheat	Millet II	Millet III	Weight of Air-dried Crop in 2 Pots	Number of Plants in 2 Pots
4	N K L	None	15	7	12	26	6	21*	45	10	25	5	14	5
2	N P 1/2 K L	Slag A	16	6	12	34	9	12	70	13	36	10	18	8
2	"	Slag B	34	78	15	32	20	29	83	13	34	9	18	8
2	"	Slag C	29	83	16	33	21	27	88	11	32	8	15	8
2	"	Slag D	39	8	15	29	25	32	55	11	32	10	14	6
2	"	Acid phosphate	50	65	17	32	7	45	44	11	35 <sup>b</sup>	8	13 <sup>a</sup>	4
2	"	Rock phosphate	12	59	15	30	9	12 <sup>b</sup>	64	16	34	10	3	3
2	"	Sodium phosphate	53	77	16	28	17	37	75	15	33	9	12	3
2	"	Double superphosphate	48	8	13	25	25	35	94	19	38	10	15	5
2	N P K L	Slag A	49	91	17	38	10	39	87	16	37	10	28	8
2	"	Slag B	42	84	18	34	10	34	98	16	37	10	15	5
2	"	Slag C	25	6	22	39	16	44	8	17	35	10	16	6
2	"	Slag D	54	104	19	36	17	43	92	14	39	10	8	8
2	"	Acid phosphate	17	79	17	38	10	34	97	18	34	10	33	8
2	"	Rock phosphate	13	84	16	35	11	20	91	16	36	9	32	8
2	"	Sodium phosphate	85	8	17	38	10	77	121	22	38	10	32	8
2	"	Double superphosphate	69	65	15	32	10	78 <sup>b</sup>	52	13	37	10	18	8
2	N P K Lx	Sodium phosphate	70	8	22	38	14	37	75	17	34	9	18	8
2	N 1 1/2 P K 1 1/2 L	Sodium phosphate	82	63	14	17	6	72 <sup>b</sup>	124	20	40	10	17 <sup>a</sup>	4
2	N P 1 1/2 K L	Sodium phosphate	78	106	21	39	10	79	144	23	35	10	32	8
2	N P 2 K L	Rock phosphate	90	8	16	35	10	42	121	21	38	10	23	8

\*Average weight from two pots based on weights taken from three pots.

<sup>b</sup>Double the weight from one pot.<sup>c</sup>One pot without plants.

TABLE 2.

*Hawaii Experiment Station. Experiment II.*

(Millet I and II grown on one application of phosphoric acid. A complete fertilizer application was made before planting the third crop.)

NUMBER OF POTS EMPLOYED	FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	AFTER FALLOW				AFTER LEGUME			
			MILLET I	MILLET II	MILLET III	MILLET I	MILLET II	MILLET III		
			Weight of Dry Crop in 2 Pots	Number of Plants in 2 Pots	Weight of Dry Crop in 2 Pots	Number of Plants in 2 Pots	Weight of Dry Crop in 2 Pots	Number of Plants in 2 Pots	Weight of Dry Crop in 2 Pots	Number of Plants in 2 Pots
			gms.		gms.		gms.		gms.	
4	N K L.....	None.....	1	10	8	9	5	3	25	8
2	N P $\frac{1}{2}$ K L.....	Slag A.....	14	8	45	8	31	8	16	8
2	"	Slag B.....	19	8	42	8	50	8	18	8
2	"	Slag C.....	8	5	38	8	38	8	13	7
2	"	Slag D.....	8	6	30	8	47	8	15	7
2	"	Acid phosphate.....	24	6	24	8	41	8	25	8
2	"	Rock phosphate.....	..	..	31	9	13	4	12	4
2	"	Sodium phosphate.....	26	8	29	8	42	5	37	7
2	"	Double superphosphate.....	22	7	23	8	41	6	27	7
2	N P K L.....	Slag A.....	21	8	48	5	50	8	21	6
2	"	Slag B.....	25	8	47	6	49	8	21	7
2	"	Slag C.....	10	7	45	7	61	8	22	8
2	"	Slag D.....	7	2	41	8	55	8	19	7
2	"	Acid phosphate.....	28	7	35	8	33	4	27	8
2	"	Rock phosphate.....	6	4	36	8	9	8	11	6
2	"	Sodium phosphate.....	43	8	42	8	28	4	26	8
2	"	Double superphosphate.....	33	7	37	8	58	8	30	7
2	N P K Lx.....	Sodium phosphate.....	39	8	45	8	53	8	32	7
2	N $1\frac{1}{2}$ P K $1\frac{1}{2}$ L.....	Sodium phosphate.....	23	5	52	9	33	8	18	4
2	N P $1\frac{1}{2}$ K L.....	Sodium phosphate.....	32	7	51	8	73	8	34	8
2	N P 2 K L.....	Rock phosphate.....	..	..	39	8	30	8	12	5

\*0.2 gram

seed was harvested; it was considered that this would furnish the necessary nitrogen. The soil used contained 36,000 pounds of potassium per 2,000,000 of soil; it was thought that the green manure crop would liberate a sufficient amount of this element from its insoluble compounds in the soil.

## MASSACHUSETTS AGRICULTURAL EXPERIMENT STATION.

## POT TESTS, 1913.

The soil was taken from the Dillon Farm in 1913, transported to the Experiment Station, limed, fertilized with both nitrogen and potash fertilizers, and cropped since 1913 to deplete the phosphoric acid. The soil was medium to light glacial drift, containing 0.09 per cent acid-



Photographs of crops grown at the Hawaii Experiment Station. Those marked 5 and 6 received nitrogen, potash, and lime, but no phosphorus. The remainder of the pots shown carried their quota of nitrogen, potash, and lime, and in addition, the source and amount of phosphate indicated; pots 69 and 70, sodium phosphate,  $P^{1\frac{1}{2}}$ ; pots 125 and 126, sodium phosphate, P; pots 149 and 150, sodium phosphate,  $P^{1\frac{1}{2}}$ ; pots 29 and 30, Slag B,  $P^{\frac{1}{2}}$ ; pots 85 and 86, Slag B, P; pots 109 and 110, acid phosphate, P.





soluble  $P_2O_5$ , on the dry matter basis; depth of soil in field, about 8 inches; 92.75 per cent passed a 1 mm. sieve. The lime requirements, in terms of 33 pounds of air-dried soil, the amount that was used in each pot, was 191.45 grams of marl for L, and 202.5 grams for Lx. The marl used tested 83.36 per cent calcium carbonate. The pots used in the experiment were of zinc,  $14\frac{1}{2}$  inches high and 10 inches in diameter. The depth of the soil in the pots was from 12 to 13 inches. No subsoil was used. The nitrate of soda tested 15.48 per cent nitrogen; the dried blood tested 13.58 per cent nitrogen and 1.02 per cent phosphoric acid; and the sulfate of potash tested 26.20 per cent potassium oxide. The phosphates were applied to all the pots in amounts recommended by the committee.

Dwarf Essex rape was planted June 2 and harvested August 28 when it was thought it had reached its maximum growth. A good stand was secured on all the pots with the exception of the extra nitrogen and potash pots where injury was apparent. The plants were dried by exposure in a closed greenhouse and on paper. The drying was subsequently completed in a steam-heated oven at a low to medium temperature. From Table 7 it will be seen that Series I had for preliminary treatment the growth of soy beans, which were turned under. The soil in Series II remained fallow during this period.

#### POT TESTS, 1916.

The soil was taken from the Dillon Farm in the fall of 1915. It had been limed in 1913 at the rate of 4,248 pounds of hydrated lime per acre; had received the nitrogen and potash applications each year, as recommended by the committee; and had been cropped since 1913 to deplete the phosphorus. (For further information regarding this soil and its preliminary treatment, see "Field Experiment on Dillon Farm," which forms a part of this report.) The lime requirement of the soil, in terms of the amount to be used for each pot, was 44.55 grams of marl for L, and 55.33 grams for Lx. The chemical and mechanical composition of the soil, depth of soil in the field, depth and weight of soil per pot, and kind and dimensions of pots were the same as in the previous experiment in 1915 with dwarf Essex rape. The marl used tested 88 per cent calcium carbonate; the nitrate of soda tested 15.48 per cent nitrogen; the dried blood tested 14.10 per cent nitrogen and 0.46 per cent  $P_2O_5$ ; and the potash salt tested 26.20 per cent  $K_2O$ . Japanese millet was planted on March 3, five hills per pot, five to six seeds per hill. These were thinned to two plants per hill on March 23. The crop was harvested on May 16 when the heads were well out of sheaths. Ten good plants were present in all the pots. The plants were dried in cloth bags suspended in a closed greenhouse, and the drying was finished in a

steam-heated oven at low or medium temperature. Dry matter determinations were made later, and the results are reported in Table 8.

## POT TESTS, 1916.

The soil was taken from Experiment Station Plot 10, South Soil Test. It was a medium to fine type, of general drift origin, commonly known as Merrimac sandy loam. The plot from which this soil was taken had received annually, per acre, since 1897, 160 pounds of nitrate of soda and 160 pounds of muriate of potash. No phosphoric acid was used during this period. In 1899 and in 1904, hydrated lime was applied to the plot at the rate of one ton per acre. Hydrated lime was also applied to this plot in 1907, at the rate of one-half ton per acre, and in 1909, at the rate of one ton per acre. The crops grown on this plot

TABLE 3.  
*Illinois Agricultural Experiment Station, 1915.*

(No commercial nitrogen or potash added. Legume crop used as manure after seed was harvested.)

NUMBER OF POTS EMPLOYED	FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	AIR-DRIED CROP PER POT			
			Clover <sup>a</sup>	Millet	Soy Beans	Rape
			grams	grams	grams	grams
2	Lime 19.4 grams	None.....	38 <sup>b</sup>	72 <sup>b</sup>	38 <sup>b</sup>	37 <sup>b</sup>
1	L P ½.....	Slag A.....	62	82	61	49
1	".....	Slag B.....	54	79	65	42
1	".....	Slag C.....	58	95	60	48
1	".....	Slag D.....	58	96	55	47
1	".....	Acid phosphate.....	54	91	55	52
1	".....	Blue rock phosphate..	42	68	34	51
1	".....	Brown rock phosphate..	52	78	38	48
1	".....	Florida soft phosphate..	38	73	37	45
1	".....	Sodium phosphate.....	73	100	70	55
1	".....	Double superphosphate.	68	92	66	46
1	L P.....	Slag A.....	70	80	70	50
1	".....	Slag B.....	65	92	81	56
1	".....	Slag C.....	74	84	85	54
1	".....	Slag D.....	70	96	70	57
1	".....	Acid phosphate.....	70	104	77	51
1	".....	Blue rock phosphate....	44	73	54	44
1	".....	Brown rock phosphate....	49	81	45	46
1	".....	Florida soft phosphate....	52	63	46	48
2	".....	Sodium phosphate.....	75	104	68	71
1	".....	Apatite.....	40	73	30	50
1	L P 1½.....	Sodium phosphate.....	60	101	82	60
1	L P 2.....	Blue rock phosphate....	44	83	43	46
1	".....	Brown rock phosphate....	52	89	45	52
1	".....	Florida soft phosphate....	47	80	55	49
1	L P.....	Double superphosphate..	68	95	85	56

<sup>a</sup>Total of three crops.

<sup>b</sup>Average of two pots.

NOTE.—Apparently equal amounts of phosphoric acid were not added to all pots as the chemical composition of the rock phosphate shows it to contain 9.91 per cent more  $P_2O_5$  than does the acid phosphate, whereas the notes accompanying the results of the experiment say that 1.47 grams more of the rock phosphate than acid phosphate were used in the  $P \frac{1}{2}$  applications and 2.93 grams more in the  $P$  applications.

during the period from 1897 to 1915 were: corn, nine; mixed grass and clover, four; buckwheat, one; oats and clover, one; crimson clover, one; soy beans, one.

A mechanical analysis of the soil showed that 96.77 per cent would pass a 1 mm. sieve. In 1913 the soil showed the presence of 0.104 per cent of acid-soluble  $P_2O_5$ . The lime requirement of the soil, in terms of the amount used for each pot, was 17.01 grams of marl for L, and 25.51 grams for Lx. The pots used in the experiment were zinc, 14½ inches high and 10 inches in diameter. No subsoil was used. The depth of the soil in the pots was 12 to 13 inches, and 33 pounds of air-dried soil were used in each pot.

TABLE 4.

*Illinois Agricultural Experiment Station, 1916.*

(No commercial nitrogen or potash added. Previous legume crops worked into soil.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	AIR-DRIED CROP PER POT			
		Rape	WHEAT		
			Total Crop	Grain	Straw
		grams	grams	grams	grams
Lime, . . . . .	None . . . . .	116 <sup>a</sup>	64 <sup>a</sup>	17 <sup>a</sup>	47 <sup>a</sup>
L P ½. . . . .	Slag A . . . . .	139	82	23	59
" . . . . .	Slag B . . . . .	134	83	23	60
" . . . . .	Slag C . . . . .	144	100	25	75
" . . . . .	Slag D . . . . .	136	92	25	67
" . . . . .	Acid phosphate . . . . .	134	95	23	72
" . . . . .	Blue rock . . . . .	114	70	19	51
" . . . . .	Brown rock . . . . .	128	76	20	56
" . . . . .	Florida soft phosphate . . . . .	139	70	20	50
" . . . . .	Sodium phosphate . . . . .	176	83	25	58
" . . . . .	Double superphosphate . . . . .	147	100	30	70
L P. . . . .	Slag A . . . . .	170	82	24	58
" . . . . .	Slag B . . . . .	132	80	23	57
" . . . . .	Slag C . . . . .	134	81	24	57
" . . . . .	Slag D . . . . .	124	82	23	59
" . . . . .	Acid phosphate . . . . .	147	96	25	71
" . . . . .	Blue rock . . . . .	134	70	19	51
" . . . . .	Brown rock . . . . .	146	76	20	56
" . . . . .	Florida soft phosphate . . . . .	128	71	21	50
" . . . . .	Sodium phosphate . . . . .	183	95	26	69
" . . . . .	Sodium phosphate <sup>b</sup> . . . . .	210	100	28	72
" . . . . .	Apatite . . . . .	129	78	23	55
L P 1½. . . . .	Sodium phosphate . . . . .	161	105	29	76
L P 2. . . . .	Blue rock . . . . .	148	80	21	59
" . . . . .	Brown rock . . . . .	135	85	24	61
" . . . . .	Florida soft phosphate . . . . .	136	90	24	66
L P. . . . .	Double superphosphate . . . . .	150	98	31	67
" . . . . .	Birmingham slag . . . . .	122	105	25	80

<sup>a</sup>Average of two pots; one pot employed on each of the other tests.

<sup>b</sup>With extra lime.

NOTE.—Apparently equal amounts of phosphoric acid were not added to all pots as the chemical composition of the rock phosphate shows it to contain 9.91 per cent more  $P_2O_5$  than does the acid phosphate, whereas in the notes accompanying results of the experiment 2.10 grams more of the rock phosphate than acid phosphate were used in the  $P\frac{1}{2}$  applications and 4.395 grams more in the P applications.

The different fertilizers used tested as follows: marl, 88 per cent calcium carbonate; nitrate of soda, 15.48 per cent nitrogen; red dried blood, 14.10 per cent nitrogen and 0.46 per cent  $P_2O_5$ ; low grade sulfate of potash, 26.20 per cent  $K_2O$ . The phosphates were applied to all the pots in amounts recommended by the committee.

The crop grown in this experiment was dwarf Essex rape, planted March 3, five hills per pot, thinned to one plant per hill on March 23. The crop was harvested May 18 when the plants had reached their maximum growth. The plants were dried in a closed greenhouse by spreading on paper, the drying being completed in a steam oven at medium temperature. A detailed report as to the condition of the crop at various stages of growth is available, but is not given here on account of the desire to make the report as brief as possible. At the time of

TABLE 5.  
*Illinois Agricultural Experiment Station, 1916.*

(No commercial nitrogen or potash added. Weights given are a total of two crops, both of clover and soy beans.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	AIR-DRIED CROP PER POT	
		Clover	Soy Beans—Total Crop
		<i>grams</i>	<i>grams</i>
Lime . . . . .	None	62	104
L P $\frac{1}{2}$ . . . . .	Slag A	86	119
" . . . . .	Slag B	85	133
" . . . . .	Slag C	55	130
" . . . . .	Slag D	83	124
" . . . . .	Acid phosphate	85	127
" . . . . .	Blue rock	54	117
" . . . . .	Brown rock	54	120
" . . . . .	Florida soft phosphate	51	101
" . . . . .	Sodium phosphate	98	124
" . . . . .	Double superphosphate	84	100
L P . . . . .	Slag A	80	125
" . . . . .	Slag B	97	140
" . . . . .	Slag C	94	128
" . . . . .	Slag D	97	123
" . . . . .	Acid phosphate	100	119
" . . . . .	Blue rock	53	111
" . . . . .	Brown rock	63	108
" . . . . .	Florida soft phosphate	60	109
" . . . . .	Sodium phosphate	107	110
" . . . . .	Sodium phosphate*	84	130
" . . . . .	Apatite	55	98
L P $1\frac{1}{2}$ . . . . .	Sodium phosphate	94	116
L P 2 . . . . .	Blue rock	55	101
" . . . . .	Brown rock	54	115
" . . . . .	Florida soft phosphate	66	111
L P . . . . .	Double superphosphate	94	128
" . . . . .	Birmingham slag	109	125

\*With extra lime.

NOTE.—Apparently equal amounts of phosphoric acid were not added to all pots as the chemical composition of the rock phosphate shows it to contain 9.91 per cent more  $P_2O_5$  than does the acid phosphate, whereas in the notes accompanying results of the experiment 1.47 grams more of the rock phosphate than acid phosphate were used in the  $P \frac{1}{2}$  applications and 2.93 grams more in the P applications.

harvesting, five good plants were present in all the pots with the exception of N 1  $\frac{1}{2}$  P K 1  $\frac{1}{2}$  L, which had only three plants. There was evidence that the additional amount of nitrogen and potash in these pots was unfavorable to the growth of rape.

From the summary, Table 9, it will be seen that Series I had for preliminary treatment the growth of soy beans, which were turned under. The soil in Series II remained fallow during the period in which the soil in Series I was used for growing the soy beans.

## FIELD EXPERIMENT.

*Preliminary treatment, 1913.*

The field selected for this experiment is on what is known as the Dillon Farm on East Pleasant Street, Amherst. It had not been plowed

TABLE 6.

*Illinois Agricultural Experiment Station, 1917.*

(No commercial nitrogen or potash added.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	AIR-DRIED CROP PER POT					
		Rape	Soy Bean Hay	Clover Hay	Wheat		
					Total Crop	Grain	Straw
		grams	grams	grams	grams	grams	grams
Lime.	None	73	87	23	66	19	47
L P $\frac{1}{2}$	Slag A.	101	92	37	73	22	51
"	Slag B.	91	89	61	92	25	67
"	Slag C.	95	81	34	91	27	64
"	Slag D.	85	92	38	90	26	64
"	Acid phosphate	100	87	64	96	24	72
"	Blue rock . . .	80	83	62	66	22	44
"	Brown rock . . .	103	86	60	73	24	49
"	Florida soft phosphate	89	89	51	74	22	52
"	Sodium phosphate	90	87	70	87	17	70
"	Double superphosphate	80	97	117	95	22	73
L P	Slag A.	91	79	100	72	22	50
"	Slag B.	116	87	55	85	23	62
"	Slag C.	105	85	75	70	18	52
"	Slag D.	115	75	57	84	22	62
"	Acid phosphate . . .	107	82	64	97	23	74
"	Blue rock . . . . .	86	74	60	62	18	44
"	Brown rock . . . . .	113	75	89	72	23	49
"	Florida soft phosphate . .	104	80	82	61	19	42
"	Sodium phosphate . . . .	109	88	124	101	22	79
"	Sodium phosphate* . . . .	151	89	91	112	30	82
"	Apatite . . . . .	79	84	30	80	26	54
"	Double superphosphate . .	108	96	104	113	29	84
L P 1 $\frac{1}{2}$	Sodium phosphate . . . .	103	103	115	98	30	68
"	Blue rock . . . . .	107	82	52	70	24	46
"	Brown rock . . . . .	117	97	90	88	28	60
"	Florida soft phosphate . .	87	85	117	70	31	39
"	Birmingham slag . . . . .	96	89	112	86	19	67
"	Ammonium phosphate . . .	189	97	130	103	22	81

\*With extra lime.

TABLE 7.

*Massachusetts Agricultural Experiment Station, 1915.*(Soil from Dillon Farm, cropped since 1913 to deplete the  $P_2O_5$ . Crop: Dwarf Essex Rape.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	SERIES I, GREEN CROP SOY BEANS TURNED UNDER		SERIES II, FALLOW	
		Yield of Dry Matter per Pot	$P_2O_5$ in Total Dry Matter per Pot	Yield of Dry Matter per Pot	$P_2O_5$ in Total Dry Matter per Pot
		<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
N K L. ....	None. ....	136	0.67	135	0.66
" " " " " "	" " " " " "	144		147	
" " " " " "	" " " " " "	129	0.60	139	0.69
" " " " " "	" " " " " "	150		135	
N P $\frac{1}{2}$ K L	Slag A. ....	152	0.85	147	0.83
" " " " " "	" " " " " "	145		150	
" " " " " "	Slag B. ....	150	0.88	160	0.83
" " " " " "	" " " " " "	155		143	
" " " " " "	Slag C. ....	149	0.69	142	0.89
" " " " " "	" " " " " "	135		139	
" " " " " "	Slag D. ....	145	0.71	141	0.78
" " " " " "	" " " " " "	140		142	
" " " " " "	Acid phosphate. ....	133	0.75	158	0.77
" " " " " "	" " " " " "	141		151	
" " " " " "	Phosphate rock. ....	141	0.63	141	0.74
" " " " " "	" " " " " "	137		134	
" " " " " "	Sodium phosphate. ....	158	0.90	169	0.98
" " " " " "	" " " " " "	160		157	
" " " " " "	Double superphosphate. ....	160	0.82	155	0.85
" " " " " "	" " " " " "	130		143	
N P K L. ....	Slag A. ....	163	0.88	168	1.01
" " " " " "	" " " " " "	160		153	
" " " " " "	Slag B. ....	168	1.00	159	0.91
" " " " " "	" " " " " "	154		159	
" " " " " "	Slag C. ....	153	1.02	171	0.93
" " " " " "	" " " " " "	162		138	
" " " " " "	Slag D. ....	161	0.97	149	0.97
" " " " " "	" " " " " "	151		162	
" " " " " "	Acid phosphate. ....	164	0.93	157	0.82
" " " " " "	" " " " " "	152		149	
" " " " " "	Phosphate rock. ....	134	0.69	143	0.64
" " " " " "	" " " " " "	139		139	
" " " " " "	Sodium phosphate. ....	160	1.07	160	1.20
" " " " " "	" " " " " "	156		151	
" " " " " "	Double superphosphate. ....	147	0.89	155	1.00
" " " " " "	" " " " " "	142		150	
N P K Lx. ....	Sodium phosphate. ....	158	1.05	143	1.16
" " " " " "	" " " " " "	154		164	
N $1\frac{1}{2}$ P K $1\frac{1}{2}$ L	Sodium phosphate. ....	27	0.39	128	0.88
" " " " " "	" " " " " "	90		121	
N P $1\frac{1}{2}$ K L	Sodium phosphate. ....	155	1.25	155	1.23
" " " " " "	" " " " " "	162		162	
N P 2 K L. ....	Phosphate rock. ....	129	0.67	121	0.73
" " " " " "	" " " " " "	126		160	

NOTE.—The above results are not used in the summary tables as the small difference in yields between the phosphate and no-phosphate pots indicates that the soil was not properly depleted of phosphorus before the experiment was run.

TABLE 8.

*Massachusetts Agricultural Experiment Station, 1916.*(Soil from Dillon Farm, cropped since 1913 to deplete the  $P_2O_5$  Crop: Japanese millet.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	YIELD OF DRY MATTER PER POT	$P_2O_5$ IN TOTAL DRY MATTER PER POT
		grams	grams
N K L . . . . .	None . . . . .	6	0.09
" . . . . .	" . . . . .	8	
" . . . . .	" . . . . .	6	0.08
" . . . . .	" . . . . .	5	
N P $\frac{1}{2}$ K L . . . . .	Slag A . . . . .	16	0.24
" . . . . .	" . . . . .	18	
" . . . . .	Slag B . . . . .	18	0.23
" . . . . .	" . . . . .	17	
" . . . . .	Slag C . . . . .	14	0.21
" . . . . .	" . . . . .	17	
" . . . . .	Slag D . . . . .	17	0.22
" . . . . .	" . . . . .	16	
" . . . . .	Acid phosphate . . . . .	17	0.21
" . . . . .	" . . . . .	18	
" . . . . .	Phosphate rock . . . . .	5	0.06
" . . . . .	" . . . . .	5	
" . . . . .	Sodium phosphate . . . . .	32	0.40
" . . . . .	" . . . . .	30	
" . . . . .	Double superphosphate . . . . .	16	0.26
" . . . . .	" . . . . .	19	
N P K L . . . . .	Slag A . . . . .	22	0.33
" . . . . .	" . . . . .	25	
" . . . . .	Slag B . . . . .	29	0.36
" . . . . .	" . . . . .	28	
" . . . . .	Slag C . . . . .	22	0.34
" . . . . .	" . . . . .	24	
" . . . . .	Slag D . . . . .	22	0.32
" . . . . .	" . . . . .	24	
" . . . . .	Acid phosphate . . . . .	27	0.36
" . . . . .	" . . . . .	28	
" . . . . .	Phosphate rock . . . . .	5	0.07
" . . . . .	" . . . . .	9	
" . . . . .	Sodium phosphate . . . . .	32	0.57
" . . . . .	" . . . . .	29	
" . . . . .	Double superphosphate . . . . .	27	0.41
" . . . . .	" . . . . .	26	
N P K Lx . . . . .	Sodium phosphate . . . . .	20	0.44
" . . . . .	" . . . . .	32	
N $1\frac{1}{2}$ P K $1\frac{1}{2}$ L . . . . .	Sodium phosphate . . . . .	19	0.41
" . . . . .	" . . . . .	22	
N P $1\frac{1}{2}$ K L . . . . .	Sodium phosphate . . . . .	35	0.67
" . . . . .	" . . . . .	38	
N P 2 K L . . . . .	Phosphate rock . . . . .	6	0.08
" . . . . .	" . . . . .	6	



TABLE 9.  
*Massachusetts Agricultural Experiment Station, 1916.*  
 (Soil from South Soil Test. Crop: Dwarf Essex Rape.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	GREEN CROP SOY BEANS TURNED UNDER, SERIES I		FALLOW, SERIES II	
		Yield of Dry Matter per Pot	P <sub>2</sub> O <sub>5</sub> in Total Dry Matter per Pot	Yield of Dry Matter per Pot	P <sub>2</sub> O <sub>5</sub> in Total Dry Matter per Pot
		<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
N K L <sup>a</sup> . . . . .	None . . . . .	42	0.55	33	0.56
" . . . . .	" . . . . .	38		44	
" . . . . .	" . . . . .	35	0.48	38	0.55
" . . . . .	" . . . . .	37		38	
N P $\frac{1}{2}$ K L <sup>a</sup> . . . . .	Slag A . . . . .	75	1.02	83	1.01
" . . . . .	" . . . . .	75		77	
" . . . . .	Slag B . . . . .	72	1.06	70	1.05
" . . . . .	" . . . . .	70		71	
" . . . . .	Slag C . . . . .	73	0.97	71	0.93
" . . . . .	" . . . . .	70		57	
" . . . . .	Slag D . . . . .	64	0.93	70	1.00
" . . . . .	" . . . . .	66		62	
" . . . . .	Acid phosphate . . . . .	69	0.91	72	1.06
" . . . . .	" . . . . .	73		67	
" . . . . .	Phosphate rock . . . . .	33	0.53	37	0.60
" . . . . .	" . . . . .	40		38	
" . . . . .	Sodium phosphate . . . . .	69	1.03	80	1.19
" . . . . .	" . . . . .	68		79	
" . . . . .	Double superphosphate . . . . .	65	0.91	66	0.92
" . . . . .	" . . . . .	60		56	
N P K L . . . . .	Slag A . . . . .	83	1.44	77	1.35
" . . . . .	" . . . . .	95		79	
" . . . . .	Slag B . . . . .	74	1.32	77	1.31
" . . . . .	" . . . . .	81		87	
" . . . . .	Slag C . . . . .	89	1.26	97	1.29
" . . . . .	" . . . . .	73		74	
" . . . . .	Slag D . . . . .	79	1.28	81	1.19
" . . . . .	" . . . . .	85		79	
" . . . . .	Acid phosphate . . . . .	83	1.24	74	1.22
" . . . . .	" . . . . .	91		78	
" . . . . .	Phosphate rock . . . . .	47	0.57	45	0.67
" . . . . .	" . . . . .	33		40	
" . . . . .	Sodium phosphate . . . . .	95	1.55	85	1.59
" . . . . .	" . . . . .	98		96	
" . . . . .	Double superphosphate . . . . .	88	1.21	80	1.06
" . . . . .	" . . . . .	93		72	
N P K Lx . . . . .	Sodium phosphate . . . . .	104	1.56	95	1.54
" . . . . .	" . . . . .	98		92	
N 1 $\frac{1}{2}$ P K 1 $\frac{1}{2}$ L <sup>b</sup> . . . . .	Sodium phosphate . . . . .	66	0.83	25	0.25
" . . . . .	" . . . . .	16		2	
N P $\frac{1}{2}$ K L . . . . .	Sodium phosphate . . . . .	107	1.85	95	1.80
" . . . . .	" . . . . .	102		93	
N P 2 K L . . . . .	Phosphate rock . . . . .	46	0.69	49	0.86
" . . . . .	" . . . . .	42		56	

<sup>a</sup>Rape roots from one pot in each case in Series I:

N K L . . . . .	None . . . . .	20	0.12		
N P $\frac{1}{2}$ K L . . . . .	Slag A . . . . .	53	0.30		
" . . . . .	Acid phosphate . . . . .	39	0.23		
" . . . . .	Phosphate rock . . . . .	12	0.08		
" . . . . .	Sodium phosphate . . . . .	27	0.17		

<sup>b</sup>Only three plants in both series.

<sup>c</sup>Five plants in Series I; two were very small. Three plants in Series II.

NOTE.—All pots had 5 plants at time of harvest, with the exceptions noted.

or fertilized for many years, and a very light crop of inferior hay had been annually harvested. The soil is a medium to light glacial drift, having the following composition, basis 100 parts of dry soil<sup>1</sup>:

	<i>Per cent</i>
Phosphoric acid..	0.09
Calcium oxide .	0.81
Potassium oxide	0.13
Nitrogen..	0.23
Humus . .	3.16
Humus nitrogen .	0.21

The area was plowed in the fall of 1912 and laid off the following spring according to the blue print prepared by the Basic Slag Committee. Based on a lime requirement test by the Veitch method, the whole area except the no-lime plots, 1 and 40, was limed at the rate of 4247.8 pounds of hydrated lime per acre, and the lime was wheel-harrowed in. The extra lime plot received 14 pounds (420 pounds per acre) more than the general lime application. The total area, with the exception of plots 1 and 40, which received no fertilizer, received the following application per acre: nitrate of soda, 200 pounds; dried blood, 600 pounds; high grade sulfate of potash, 500 pounds. To the plot that was to receive the liberal application of phosphoric acid, acid phosphate was applied at the rate of 600 pounds per acre.

After good tilth was established, Davis yellow flint corn was planted May 27 and 28. An even stand was secured on all the area. The corn was harvested September 15. The yields of dry matter per acre are shown in Table 10.

#### 1914.

The soil was harrowed May 5; fitted May 19; fertilized with the same nitrogen and potash applications as for the previous year; and sowed

TABLE 10.  
*Yield of dry matter per acre reported from Massachusetts.*

PLOTS	SOUND CORN— DRY MATTER CORN AND COB	UN SOUND CORN— DRY MATTER CORN AND COB	STOVER DRY MATTER	TOTAL DRY MATTER
	<i>pounds</i>	<i>pounds</i>	<i>pounds</i>	<i>pounds</i>
2-39, inclusive (nitrogen and potash)	2025	634	3118	5776
1, no fertilizer	1798	602	2997	5397
40, no fertilizer	1438	1139	2927	5504
Phosphoric acid in addition to nitrogen and potash	468	439	1803	2710
Extra lime with nitrogen and potash	383	293	1639	2315

<sup>1</sup> Other elements were determined, but for the sake of brevity are not included in this report.

to oats, two bushels per acre. A good stand was secured. The oats were harvested August 4.

PLOTS	DRY MATTER PER ACRE
	<i>pounds</i>
2-39, inclusive (nitrogen and potash)...	5293
1, no fertilizer .....	3796
40, no fertilizer .....	3175
Phosphoric acid, nitrogen, and potash..	5750
Nitrogen, potash, and extra lime.....	4878

The land was fitted August 11 and 12 and sowed to buckwheat. An even stand was secured over the whole area. The buckwheat was harvested September 28.

PLOTS	DRY MATTER PER ACRE
	<i>pounds</i>
2-39, inclusive (nitrogen and potash)...	837
1, no fertilizer .....	1652
40, no fertilizer .....	1102
Phosphoric acid, nitrogen, and potash..	723
Nitrogen, potash, and extra lime....	413

### 1915.

The land was plowed in early April and fitted April 22. The same nitrogen and potash fertilizers were applied as in 1913. Clydesdale oats were sown, and the stand over the whole area was good. The crop, which was harvested July 30, had not made as good growth as in the previous year.

PLOTS	DRY MATTER PER ACRE
	<i>pounds</i>
2-39, inclusive (nitrogen and potash)...	4270
1, no fertilizer .....	3127
40, no fertilizer .....	2408
Nitrogen, potash, and phosphoric acid..	3501
Nitrogen, potash, and extra lime.....	2317

The land was fitted August 17 and sowed to Japanese buckwheat. A good stand was secured over the whole area. The crop was harvested October 25.

PLOTS	DRY MATTER PER ACRE
	<i>pounds</i>
2-39, inclusive (nitrogen and potash)...	1844
1, no fertilizer .....	1860
40, no fertilizer .....	1400
Nitrogen, potash, and phosphoric acid..	1973
Nitrogen, potash, and extra lime.....	1230

## 1916.

The land was fitted May 15. Nitrogen and potash fertilizers were applied as in previous years and, in addition, phosphoric acid compounds according to the fertilizer schedule of the Basic Slag Committee. Although it was apparent that the soil had not been sufficiently depleted in phosphorus by the preliminary treatment, it was thought best to run the final experiment as the lease to the land expired during the year. Dwarf Essex rape was sown June 8 in drills one foot apart, 11 rows per plot. A poor stand was secured, apparently due to poor seed. On June 27 and 28 the land was again harrowed and seeded. A good stand was secured on all the plots, and good growth, except on plots 1 and 40 where no fertilizer was used. The crop was harvested September 8. On plot 1, about 45 per cent of the total weight was weeds and grasses, and on plot 40, about 50 per cent. The other plots were practically free from weeds and grasses.

## NEW JERSEY AGRICULTURAL EXPERIMENT STATION.

## POT EXPERIMENTS.

*Series I.*—Earthenware pots, holding 20 pounds of white quartz sand, were used. The general fertilizer treatment was as follows: each pot received 4 grams of potassium sulfate, 3 grams of sodium nitrate, 5 grams of calcium carbonate,  $\frac{1}{2}$  gram of magnesium sulfate, and  $\frac{1}{4}$  gram of ferric sulfate. The phosphorus treatment was based on the use of 6 grams of acid phosphate as the standard, and sufficient amounts of the other phosphates were used to give an equivalent in phosphoric acid. The experiment was conducted in the greenhouse in the winter of 1913–1914. Moisture was maintained at about 10 per cent. Barley was the crop grown.

*Series II.*—The same kind and size pots, and same weight of quartz sand, were used as in Series I. The general fertilizer treatment was as follows: 2 grams of potassium chloride, 2 grams of sodium nitrate, 10 grams of ground limestone,  $\frac{1}{2}$  gram of magnesium sulfate, and  $\frac{1}{4}$  gram of ferric sulfate. The phosphorus treatment was somewhat reduced from Series I: 4 grams of acid phosphate were taken as the standard for  $P\frac{1}{2}$ , and sufficient amounts of the other phosphates were used to give an equivalent in phosphoric acid. Slag E, included in this series and in Series III, was an American product prepared at Birmingham, Alabama, testing 18.33 per cent phosphoric acid. Moisture was maintained at about 10 per cent. The experiment was conducted in the greenhouse. The crop grown was buckwheat.

*Series III.*—The plan of this experiment was identical with that of Series II, except that 1 gram of nitrate of soda was used instead of two. The crop grown was soy beans, planted April 26 and harvested as forage on August 27.

TABLE 11.

*Massachusetts Agricultural Experiment Station, 1916. Field Experiment.*(Soil on Dillon Farm, cropped since 1913 to deplete  $P_2O_5$ . Crop: Dwarf Essex Rape.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	YIELD OF DRY MATTER PER PLOT	$P_2O_5$ IN TOTAL DRY MATTER PER PLOT
		<i>pounds</i>	<i>pounds</i>
Nothing . . . . .	None . . . . .	17	0.08
" . . . . .	" . . . . .	15	0.08
N K L . . . . .	None . . . . .	46	0.36
" . . . . .	" . . . . .	51	0.29
N P $\frac{1}{2}$ K L . . . . .	Slag A. . . . .	37	0.24
" . . . . .	" . . . . .	62	0.35
" . . . . .	Slag B. . . . .	46	0.29
" . . . . .	" . . . . .	55	0.36
" . . . . .	Slag C. . . . .	48	0.34
" . . . . .	" . . . . .	48	0.26
" . . . . .	Slag D. . . . .	49	0.30
" . . . . .	" . . . . .	48	0.28
" . . . . .	Acid phosphate . . . . .	55	0.39
" . . . . .	" . . . . .	51	0.35
" . . . . .	Phosphate rock . . . . .	45	0.31
" . . . . .	" . . . . .	63	0.37
" . . . . .	Sodium phosphate . . . . .	50	0.30
" . . . . .	" . . . . .	58	0.34
" . . . . .	" . . . . .	57	0.36
N P K L . . . . .	Slag A. . . . .	74	0.45
" . . . . .	" . . . . .	58	0.50
" . . . . .	Slag B. . . . .	49	0.31
" . . . . .	" . . . . .	60	0.41
" . . . . .	Slag C. . . . .	52	0.34
" . . . . .	" . . . . .	65	0.41
" . . . . .	Slag D. . . . .	57	0.36
" . . . . .	" . . . . .	59	0.41
" . . . . .	Acid phosphate . . . . .	61	0.39
" . . . . .	" . . . . .	55	0.33
" . . . . .	Phosphate rock . . . . .	59	0.38
" . . . . .	" . . . . .	55	0.31
" . . . . .	Sodium phosphate . . . . .	60	0.41
" . . . . .	" . . . . .	65	0.49
" . . . . .	" . . . . .	50	0.34
N P K Lx . . . . .	Sodium phosphate . . . . .	57	0.38
" . . . . .	" . . . . .	55	0.37
N P 1 $\frac{1}{2}$ K L . . . . .	Sodium phosphate . . . . .	63	0.47
" . . . . .	" . . . . .	63	0.54
N 1 $\frac{1}{2}$ P K 1 $\frac{1}{2}$ L . . . . .	Sodium phosphate . . . . .	55	0.37
" . . . . .	" . . . . .	59	0.40
N P 1 $\frac{1}{2}$ K L <sup>a</sup> . . . . .	Acid phosphate . . . . .	59	0.42
N K Lx <sup>b</sup> . . . . .	None . . . . .	26	0.13

<sup>a</sup>Plot 1/30 acre received 20 pounds of acid phosphate annually, besides nitrogen and potash. Results are tabulated on basis of 1/50 acre fertilized and 1/80 acre harvested.<sup>b</sup>Plot 1/30 acre received nitrogen and potash each year and an extra lime application (4621.8 pounds per acre). Results are tabulated on basis of 1/80 acre harvested.

Table 12 gives the yields of dry matter in the three series.

*Pot Experiment No. 8.*—Glazed earthenware pots were used, containing 20 pounds each of white sand practically devoid of plant food. The general fertilizer treatment consisted of 4 grams of high-grade sulfate of potash, 3 grams of nitrate of soda, 5 grams of carbonate of lime,  $\frac{1}{2}$  gram of magnesium sulfate, and  $\frac{1}{4}$  gram of ferric sulfate. The phosphorus treatment was based on the use of 6 grams of acid phosphate as the standard, and sufficient amounts of the other phosphates were used to give an equivalent in phosphoric acid. Moisture was maintained at about 10 per cent. Buckwheat was sown June 28 and harvested August 22. when the grain was beginning to ripen.

*Pot Experiment No. 9.*—Glazed earthenware pots were used, containing 18 pounds of gravelly loam, poor in nitrogen and organic matter and containing 0.07 per cent of phosphoric acid soluble in strong hydrochloric acid. The general fertilizer treatment and phosphoric acid applications were the same as in the previous experiment, No. 8. Moisture was maintained at about 15 per cent. Buckwheat was sown

TABLE 12.

*New Jersey Agricultural Experiment Station. Winter of 1913-1914.*

(On white quartz sand. Series I: crop, barley. Series II. crop, buckwheat Series III: crop, soy beans.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	SERIES I	SERIES II	SERIES III
		Yield of Dry Matter per Pot	Yield of Dry Matter per Pot	Yield of Dry Matter per Pot
		grams	grams	grams
N K L.	None	2	3	9
"	"	2	3	13
"	"	7	3	10
"	"	6	3	8
N P $\frac{1}{2}$ K L	Slag A	9	17	12
"	"	11	16	17
"	Slag B	9	20	26
"	"	12	17	18
"	Slag C	8	17	17
"	"	10	20	25
"	Slag D	9	19	16
"	"	10	18	18
"	Slag E	19	19	25
"	"	18	18	19
"	Acid phosphate	10	23	28
"	"	10	21	30
"	Sodium phosphate	"	8	27
"	"	"	5	32
"	Double superphosphate	15	11	38
"	"	15	18	35
N P K L	Slag E	16	16	25
"	"	19	19	25
"	Blue rock phosphate	6	7	8
"	"	6	10	10

\*0.3 gram.

June 28 and harvested August 22, when the grain was beginning to ripen. Dry matter weights are given in Table 13.

CORNELL UNIVERSITY AGRICULTURAL EXPERIMENT STATION.

POT WORK, 1913.

The soil was Dunkirk clay loam. In the spring a crop of barley was grown to exhaust the soil of phosphorus. After the barley was harvested the soil was prepared, and the following general fertilizers were added: for N, nitrate of soda 2.8 grams, dried blood 8.3 grams; for K, sulfate of potash 6.9 grams. Carbonate of lime was not used except in case of N P K L sodium phosphate, as shown in Table 14. The table showing yields also gives the source of each phosphate, the amounts employed being based on the use of 0.69 gram of acid phosphate for P  $\frac{1}{2}$ ; sufficient amounts of the other phosphates were used to give an equivalent in phosphoric acid. The pots were three-gallon glazed earthenware, 10 inches deep and 10 inches in diameter. Each pot contained 15 kilos of soil. The moisture content of the soil was maintained uniform during the growth of the plants. Rape was planted June 10 and later thinned to 10 plants per pot. The crop was harvested September 12. The yields are expressed in terms of dry matter.

TABLE 13.

*New Jersey Agricultural Experiment Station, 1913.*

(Results of Pot Experiment No. 8 on white sand and No. 9 on gravelly loam. Crop grown: Buckwheat.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	EXPERIMENT No. 8.	EXPERIMENT No. 9.
		Yield of Dry Matter per Pot	Yield of Dry Matter per Pot
		<i>grams</i>	<i>grams</i>
N K L . . . . .	None . . . . .	3	23
" . . . . .	" . . . . .	3	26
" . . . . .	" . . . . .	3	24
" . . . . .	" . . . . .	2	23
N P $\frac{1}{2}$ K L . . . . .	Slag A . . . . .	14	33
" . . . . .	" . . . . .	15	30
" . . . . .	Slag B . . . . .	12	33
" . . . . .	" . . . . .	21	37
" . . . . .	Slag C . . . . .	15	28
" . . . . .	" . . . . .	15	28
" . . . . .	Slag D . . . . .	17	40
" . . . . .	" . . . . .	14	27
" . . . . .	Acid phosphate . . . . .	17	31
" . . . . .	" . . . . .	16	30
" . . . . .	Sodium phosphate . . . . .	3	29
" . . . . .	" . . . . .	4	31
" . . . . .	Double superphosphate . . . . .	19	33
" . . . . .	" . . . . .	17	31
N P K L . . . . .	Blue rock phosphate . . . . .	10	24
" . . . . .	" . . . . .	10	25

## POT WORK, 1914.

The soil used was the same as for the previous experiment. After the crop of rape was harvested the soil was removed from the pots, the roots were sifted out, and after the soil was returned to the pots the same general fertilizers and phosphates were added as in the rape experiment. The soil was brought to a moisture content of 30 per cent and so maintained throughout the growth of the crop. Wheat was the crop grown, 12 plants per pot. The yields are recorded on the dry matter basis.

## NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION.

## POT EXPERIMENTS.

Preliminary work was begun for the basic slag pot work in the spring of 1916. The pots were glazed earthenware of four gallons capacity. Drainage facilities were provided by small openings on the lower side of each pot. The work was done out of doors in a cage of  $\frac{1}{4}$  mesh poultry wire, the pots resting on benches 2 feet above ground. Water was supplied each day when necessary to keep the soil well moistened. The soil was Cecil sandy loam about 6 inches deep and was taken from field plots 5 and 34. Each pot contained 45 pounds of dry soil which had been previously well mixed and passed through a 3 mm. sieve: 11.64 per cent failed to pass the sieve. The depth of the soil in the pots was 10 inches. Lime, at the rate of 690 pounds CaO for each 2,000,000 pounds of soil, was added to each pot on May 15. The pots in the series that received a legume as preliminary treatment were seeded with soy beans May 30 and thinned to 5 plants June 10. The pots in the series that was kept fallow during the growing of the soy beans were watered at regular intervals, and the soil was stirred to a depth of 3 inches. On September 12 and 13 the green soy beans were cut and intimately mixed with the soil in one series. The phosphatic fertilizer materials, in amounts recommended by the committee, were applied to all the pots; the nitrogen and potash fertilizers were added at various stages of plant growth; and after the specified time had elapsed, dwarf Essex rape was seeded. This crop winterkilled so that it was necessary to replant March 15, 1917. Millet was planted in another experiment July 9. In the experiment with rape, each pot contained 3 plants, and with millet, 7 plants. The rape was harvested July 4 and 5; the millet, September 20 and 21.

## NORTH DAKOTA AGRICULTURAL COLLEGE.

## POT EXPERIMENTS.

The crops used were millet, 12 plants per pot, and rape, 6 plants per pot. The soil was Fargo fine sandy loam from the McLeod Demonstra-



TABLE 14.

Cornell University Agricultural Experiment Station.

(Dunkirk clay loam on which barley was grown in spring of 1913 to deplete phosphorus.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	1913, RAPE	1914, WHEAT	
		Yield of Dry Matter— Two Pots	Straw Yield of Dry Matter— Two Pots	Grain Yield of Dry Matter— Two Pots
		<i>grams</i>	<i>grams</i>	<i>grams</i>
N K . . . . .	None . . . . .	63	130	65
" . . . . .	" . . . . .	58	126	61
N P $\frac{1}{2}$ K . . . . .	Slag A . . . . .	71	150	75
" . . . . .	" . . . . .	79	117	63
" . . . . .	Slag B . . . . .	73	135	72
" . . . . .	" . . . . .	65	127	66
" . . . . .	Slag C . . . . .	64	121	61
" . . . . .	" . . . . .	59	130	66
" . . . . .	Slag D . . . . .	67	131	67
" . . . . .	" . . . . .	65	143	74
" . . . . .	Acid phosphate . . . . .	61	128	67
" . . . . .	" . . . . .	57	140	74
" . . . . .	Rock phosphate . . . . .	59	120	65
" . . . . .	" . . . . .	52	121	60
" . . . . .	Sodium phosphate . . . . .	61	122	64
" . . . . .	" . . . . .	76	130	68
" . . . . .	" . . . . .	62	122	58
N P K . . . . .	Slag A . . . . .	63	126	68
" . . . . .	" . . . . .	87	162	80
" . . . . .	Slag B . . . . .	59	124	65
" . . . . .	" . . . . .	88	163	82
" . . . . .	Slag C . . . . .	65	114	61
" . . . . .	" . . . . .	62	133	68
" . . . . .	Slag D . . . . .	54	120	61
" . . . . .	" . . . . .	66	135	70
" . . . . .	Acid phosphate . . . . .	61	130	61
" . . . . .	" . . . . .	70	176	73
" . . . . .	Rock phosphate . . . . .	50	114	66
" . . . . .	" . . . . .	63	123	65
" . . . . .	Sodium phosphate . . . . .	73	129	62
" . . . . .	" . . . . .	76	143	70
" . . . . .	" . . . . .	71	132	61
N 1 $\frac{1}{2}$ P K 1 $\frac{1}{2}$ . . . . .	Sodium phosphate . . . . .	70	136	70
" . . . . .	" . . . . .	80	149	79
N P K L . . . . .	Sodium phosphate . . . . .	51	112	60
" . . . . .	" . . . . .	78	115	59
N P 1 $\frac{1}{2}$ K . . . . .	Sodium phosphate . . . . .	69	126	69
" . . . . .	" . . . . .	78	125	65
Nothing . . . . .	None . . . . .	21	47	18
" . . . . .	" . . . . .	20	52	21

NOTE.—The above results are not used in the summary tables as the small difference in yields between the phosphate and no-phosphate pots indicates that the soil was not properly depleted of phosphorus before the experiment was run.

tion farm, Sandoun district, Ransom County. The soil was cropped to oats in 1910, flax in 1911, and speltz in 1912. In the summer of 1913 carbonate of lime was applied at the rate of 4 grams per pot. The legume series was seeded to medium red clover, which did not make a satisfactory growth. The soil contained 0.11 per cent acid-soluble  $P_2O_5$  and 2.16 per cent calcium oxide. The depth of the soil in the field was 7 inches. The soil was found alkaline by the Veitch method; 100 per cent of the soil in the pots was finer than 1 mm. Earthenware pots  $8\frac{1}{2}$  by  $8\frac{1}{2}$  inches were used, and each contained about 7 inches of soil. In the legume series 3700 grams of air-dried soil were used in

TABLE 15.

*North Carolina Agricultural Experiment Station, 1917.*

(Pot experiment on Cecil sandy loam deficient in phosphorus.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	DWARF ESSEX RAPE		MILLET	
		AFTER LEGUME TURNED UNDER	AFTER REMAINING FALLOW	AFTER LEGUME TURNED UNDER	AFTER REMAINING FALLOW
		Yield of Dry Matter Per Pot	Yield of Dry Matter Per Pot	Yield of Dry Matter Per Pot	Yield of Dry Matter Per Pot
		grams	grams	grams	grams
N K L	None	12	8	4	..
"	"	8	10	6	.
"	"	10	12	6	4
"	"	10	.	5	3
N P $\frac{1}{2}$ K L	Slag A	74	49	34	16
"	"	80	51	34	19
"	"	70	51	36	14
"	"	74	42	30	12
"	Slag B	84	45	38	12
"	"	70	50	33	20
"	"	77	43	30	16
"	"	71	49	30	15
"	Slag C	83	38	39	16
"	"	74	45	34	17
"	"	77	43	31	20
"	"	73	48	36	14
"	Slag D	75	40	40	20
"	"	75	41	36	20
"	"	78	53	38	15
"	"	83	50	32	21
"	Acid phosphate	84	71	40	26
"	"	79	66	42	29
"	"	86	74	40	31
"	"	90	60	38	25
"	Double superphosphate	88	69	42	29
"	"	96	62	41	24
"	"	86	74	36	32
"	"	85	76	43	32
"	Phosphate rock	26	19	8	6
"	"	30	15	10	5
"	"	30	16	10	7
"	"	27	18	9	9

TABLE 15—Continued.

North Carolina Agricultural Experiment Station, 1917.

(Pot experiment on Cecil sandy loam deficient in phosphorus.)

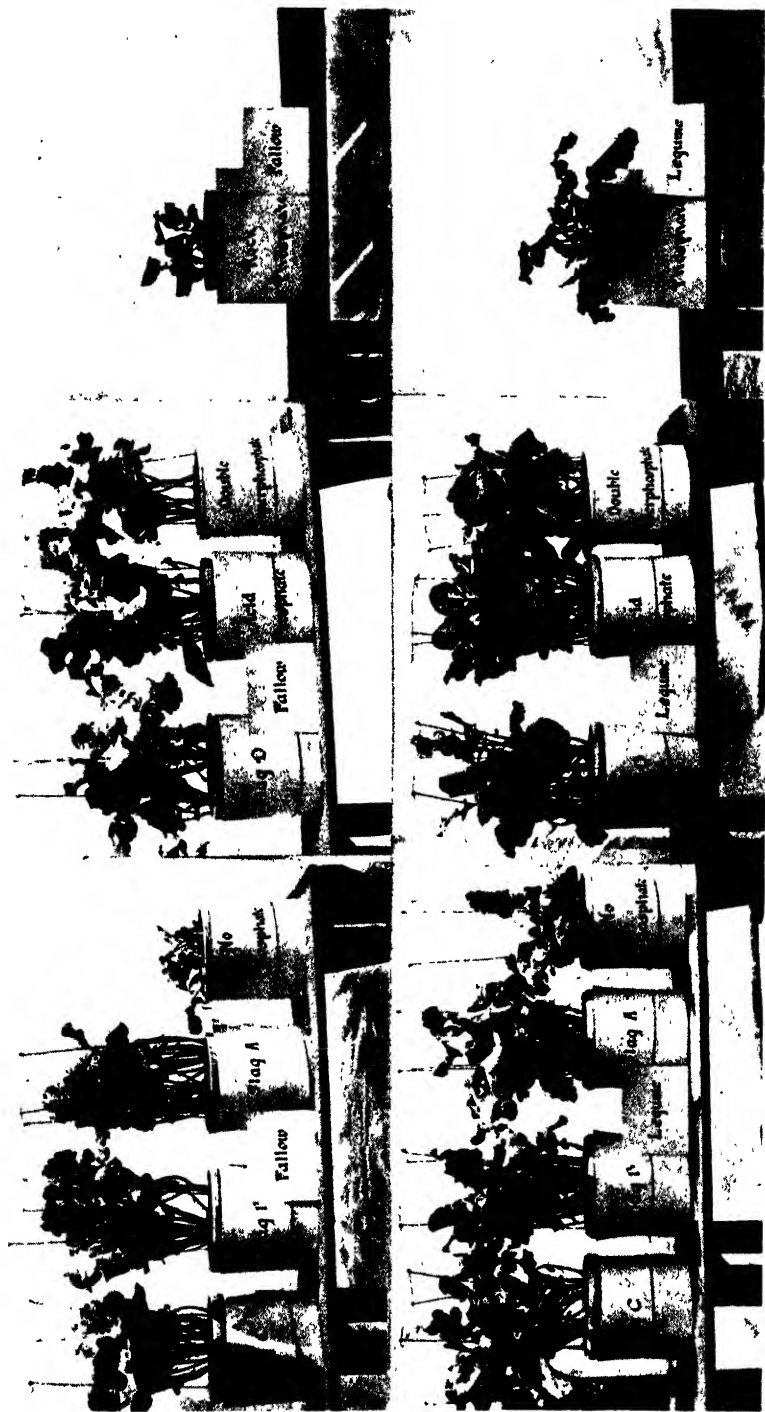
FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	DWARF ESSEX RAPE		MILLET	
		AFTER LEGUME TURNED UNDER	AFTER REMAINING FALLOW	AFTER LEGUME TURNED UNDER	AFTER REMAINING FALLOW
		Yield of Dry Matter Per Pot	Yield of Dry Matter Per Pot	Yield of Dry Matter Per Pot	Yield of Dry Matter Per Pot
		<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
N P K L...	Slag A.....	77	50	42	20
" .....	" .....	80	53	46	22
" .....	" .....	79	57	46	18
" .....	" .....	74	55	41	20
" .....	Slag B.....	73	60	40	19
" .....	" .....	80	56	40	20
" .....	" .....	73	54	46	18
" .....	" .....	75	57	38	24
" .....	Slag C.....	81	51	36	20
" .....	" .....	78	53	42	20
" .....	" .....	87	53	40	14
" .....	" .....	91	50	44	17
" .....	Slag D.....	86	52	44	18
" .....	" .....	83	49	40	21
" .....	" .....	81	50	38	16
" .....	" .....	82	55	46	19
" .....	Acid phosphate.....	90	69	50	24
" .....	" .....	88	64	46	26
" .....	" .....	92	54	48	29
" .....	" .....	91	60	43	24
" .....	Double superphosphate..	95	56	54	27
" .....	" .....	103	60	48	30
" .....	" .....	91	53	44	28
" .....	" .....	93	62	40	26
" .....	Phosphate rock.....	37	22	10	8
" .....	" .....	36	26	12	7
" .....	" .....	34	24	12	5
" .....	" .....	32	19	14	6
N P 2 K L..	Phosphate rock.....	30	22	14	10
" .....	" .....	38	25	12	8
" .....	" .....	36	23	16	9
" .....	" .....	34	25	10	7

each pot, and in the fallow series 3300 grams. The time of planting was May 9, 1914; of harvesting, August 18. The trials were completed sooner than planned as mice began to destroy the millet, and worms the rape. Note is made in Table 16 of those damaged to the greatest extent.

## PENNSYLVANIA AGRICULTURAL EXPERIMENT STATION.

## FIELD EXPERIMENT.

The soil selected was on the experimental farm and known as Hagers-town clay loam. It was in a good state of fertility, having been devoted



Photographs of representative crops grown by the North Carolina Experiment Station in co-operation with the Basic Slag Committee of A. O. A. C. to illustrate the comparative growth secured with the different phosphates in two series (legume and fallow) with Dwarf Essex Rape.



Photographs of representative crops grown by the North Carolina Experiment Station  
 in co-operation with the Basic Slag Committee of A. O. A. C. to illustrate  
 the comparative growth secured with the different phosphates  
 in two series (legume and fallow) with Millet.

to a five-year rotation of corn, oats, wheat, clover, and timothy for many years. Plots were laid out in exact conformity to the specifications of the Basic Slag Committee. The field that had been in grass for two years was manured in the fall of 1911 and plowed to a depth of 7 or 8 inches. The lime requirement of the soil was not determined; the crops previously grown did not indicate any lack of lime. On June 12, 1912, the following fertilizers were applied uniformly all over the plots except 1 and 40: nitrate of soda, 184 pounds; dried blood, 552 pounds; muriate of potash, 460 pounds. On June 15 to 19 potatoes were planted. Growth was satisfactory. There was scarcely any injury from insects. The vines were somewhat affected by early blight, but no late blight was observed. There was no apparent difference between the potatoes on the various plots; even the no-fertilizer plots seemed as good as the others. The actual yields from measured areas showed

TABLE 16.  
North Dakota Agricultural College, 1914.  
(Pot Experiment on Fargo Fine Sandy Loam.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	RAPE		MILLET	
		GROWN AFTER LEGUME	GROWN AFTER FALLOW	GROWN AFTER LEGUME	GROWN AFTER FALLOW
		Yield of Green Crop Per Pot	Yield of Green Crop Per Pot	Yield of Green Crop Per Pot	Yield of Green Crop Per Pot
		<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
N K .....	None .....	49 <sup>a</sup>	44	22	24
N K P ½ .....	Slag A .....	49	51	10	30
" .....	Slag B .....	60	56	15	14
" .....	Slag C .....	98	87	28	24
" .....	Slag D .....	52	96	20	..
" .....	Acid phosphate .....	64	104	64	42 <sup>a</sup>
" .....	Rock phosphate .....	52 <sup>b</sup>	73	12	17
" .....	Sodium phosphate .....	39 <sup>b</sup>	79 <sup>a</sup>	24	32
" .....	Double superphosphate .....	62 <sup>b</sup>	90	48	60 <sup>a</sup>
N K P .....	Slag A .....	52	98	19	22
" .....	Slag B .....	81	72	7	26
" .....	Slag C .....	95	100	12	36
" .....	Slag D .....	63	101	46	24
" .....	Acid phosphate .....	66 <sup>b</sup>	65	43 <sup>a</sup>	39
" .....	Rock phosphate .....	40 <sup>b</sup>	50	15 <sup>a</sup>	23 <sup>a</sup>
" .....	Sodium phosphate .....	70 <sup>b</sup>	132	39	44
" .....	Double superphosphate .....	81	60	41	59
N K P Lx .....	Sodium phosphate .....	102	..	103	..
N 1 ½ K 1 ½ P .....	Sodium phosphate .....	6	76	48	34 <sup>a</sup>
N K P 1 ½ .....	Sodium phosphate .....	79	..	56	..
N K P 2 .....	Rock phosphate .....	62	40	..	8

<sup>a</sup>Badly eaten by mice and insects.

<sup>b</sup>Eaten, but not so seriously.

NOTE.—These results are not used in the summary tables on account of damage to the crops by mice and insects, and because of the small difference in yields between the phosphate and no-phosphate pots.

1600 pounds more potatoes per acre where no phosphate was used than where the complete fertilizer was applied.

1913.—The land was plowed April 7. The fertilizer, which consisted of nitrate of soda, dried blood, and sulfate of potash in the amounts recommended by the committee, and the different phosphates as well, was applied June 4; the land was fitted and sown to Japanese millet. The stand was uniform and growth good. The crop was harvested August 21 to 23. The yield of air-dried millet hay is given in Table 17.

TABLE 17.  
*Pennsylvania Agricultural Experiment Station.*

(Field experiment on Hagerstown clay loam. Crops: Japanese millet 1913, dwarf Essex rape 1914, Wheat 1915.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	YIELD OF AIR-DRIED MILLET HAY PER PLOT	YIELD OF GREEN RAPE PER PLOT	YIELD OF AIR-DRIED WHEAT PER PLOT	
				Straw	Grain
		<i>pounds</i>	<i>pounds</i>	<i>pounds</i>	<i>pounds</i>
No fertilizer..	None .....	88	29	22	14
"	" .....	105	93	32	22
N K L .....	None .....	114	45	35	22
"	" .....	120	61	29	24
N P $\frac{1}{2}$ K L .....	Slag A .....	130	39	32	20
"	" .....	93	41	29	21
"	Slag B .....	116	37	29	19
"	" .....	84	41	30	21
"	Slag C .....	113	35	29	20
"	" .....	112	44	34	20
"	Slag D .....	117	35	31	20
"	" .....	106	79	34	22
"	Acid phosphate .....	128	31	33	19
"	" .....	126	86	39	23
"	Sodium phosphate .....	122	37	28	20
"	" .....	114	27	29	19
"	" .....	107	64	34	18
"	Rock phosphate .....	112	46	31	19
"	" .....	92	35	31	21
N P K L .....	Slag A .....	115	39	31	21
"	" .....	121	27	23	24
"	Slag B .....	100	21	27	18
"	" .....	106	24	30	20
"	Slag C .....	105	32	31	20
"	" .....	105	49	35	23
"	Slag D .....	99	38	32	22
"	" .....	95	34	32	23
"	Acid phosphate .....	123	35	29	19
"	" .....	117	30	31	15
"	Sodium phosphate .....	122	28	31	20
"	" .....	119	63	39	25
"	" .....	115	65	30	18
"	Rock phosphate .....	108	54	32	20
"	" .....	95	46	34	22
N P K Lx .....	Sodium phosphate .....	128	38	29	21
"	" .....	111	45	38	21
N 1 $\frac{1}{2}$ P K 1 $\frac{1}{2}$ L .....	Sodium phosphate .....	128	50	32	20
"	" .....	124	28	31	20
N P 1 $\frac{1}{2}$ K L .....	Sodium phosphate .....	122	29	33	21
"	" .....	127	61	27	19

1914.—The plots were plowed June 5; the land was fitted and sown to dwarf Essex rape June 6. No fertilizer was used. The stand was only fair, due to lack of moisture after seeding. Growth was not normal as rainfall for June, July, and August was four inches below normal for that period. The crop was cut August 27 and 28 and weighed green. Results are given in Table 17.

On September 8 the field was disked, and 300 pounds of dried blood and 200 pounds of muriate of potash were applied to the 38 plots (plots 1 and 40 were not fertilized). Phosphate fertilizers were not used on any of the plots. The field was sown to wheat. A fairly good stand was secured but growth was small, due to lack of moisture.

1915.—The stand of wheat was fair but plants were small. The wheat was harvested July 21 and 22. Yields of both grain and straw are given in the table.

#### RHODE ISLAND AGRICULTURAL EXPERIMENT STATION.

##### POT WORK.

The soil for the pot work was taken in November, 1913, from the "Underwood Land", which had been selected for the cooperative field experiment. Following the liberal application of lime and non-phosphatic fertilizer the land had produced one crop each of oats, buckwheat, and silage corn. The surface soil was taken for the experiment. Each of the Wagner pots contained about 7 inches of soil, which weighed, when oven dried, 11.36 pounds. With the exception of 1.16 per cent all the soil passed a 10-mesh sieve. Calcium carbonate was applied at the rate of 2 tons per acre (14.5 grams per pot). Crimson clover was grown as a legume to be incorporated with the soil as a preliminary treatment in one series of pots for both the rape and the millet experiments. Another series remained fallow during the growing of the legume. The general fertilizer application for each pot was as follows: 3.32 grams of nitrate of soda, 22.76 grams of dried blood, 18.6 grams of low-grade sulfate of potash, and 1 gram of  $P_2O_5$  from the various phosphorus sources for P  $\frac{1}{2}$ . The phosphates, dried blood, and 5 grams of the potash salt were mixed with the entire soil May 19 to 23; the remainder of the potash salt and all of the nitrate were added in solution during the experiment. Both the rape and the millet were planted June 3 and 4. The rape was thinned to 5 and the millet to 12 plants per pot. On September 1 to 4 the plants had attained their maximum growth and were harvested. They were dried at 60°C., and later subjected to room conditions before weighing.

It should be mentioned at this time that both the preliminary and final pot work has been completely presented by B. L. Hartwell in Bulletin 171, June, 1917, Rhode Island Agricultural Experiment Station, to which reference is made for fuller details.



TABLE 18.

*Rhode Island Agricultural Experiment Station, 1914.*(Soil from Underwood Land previously cropped to deplete the  $P_2O_5$ .)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	DWARF ESSEX RAPE			JAPANESE MILLET				
		YIELD OF AIR-DRIED RAPE			AFTER CLOVER	AFTER FALLOW			Weight of P <sub>2</sub> O <sub>5</sub> Recovered in Tops
		After Clover	After Fallow			Weight of Air-Dried Millet Tops	Weight of Air-Dried Millet		
			Tops	Roots			Tops	Roots	
		grams	grams	grams	grams	grams	grams	grams	
N K L . . . . .	None . . . . .	7	16	7	45	34	10	0.09	
“ “ “ “ “	“ “ “ “ “	14	18	7	38	31	7	0.10	
NP ½ K L . . . . .	Slag A . . . . .	103	91	29	90	70	17	0.25	
“ “ “ “ “	“ “ “ “ “	103	99	28	81	73	19	0.26	
“ “ “ “ “	Slag B . . . . .	97	77	28	88	77	25	0.24	
“ “ “ “ “	“ “ “ “ “	102	61	14	82	76	20	0.26	
“ “ “ “ “	Slag C . . . . .	105	78	21	87	76	23	0.24	
“ “ “ “ “	“ “ “ “ “	101	68	20	88	83	20	0.27	
“ “ “ “ “	Slag D . . . . .	82	68	16	92	76	36	0.23	
“ “ “ “ “	“ “ “ “ “	81	59	16	89	73	33	0.24	
“ “ “ “ “	Acid phosphate . . . . .	105	106	29	77	75	18	0.25	
“ “ “ “ “	“ “ “ “ “	110	88	23	87	82	22	0.25	
“ “ “ “ “	Double superphosphate . . . . .	109	81	34	79	77	27	0.26	
“ “ “ “ “	“ “ “ “ “	112	86	32	91	76	27	0.25	
N P K L . . . . .	Slag A . . . . .	120	120	37	109	86	19	0.32	
“ “ “ “ “	“ “ “ “ “	128	130	47	104	96	35	0.37	
“ “ “ “ “	Slag B . . . . .	115	127	26	104	93	32	0.32	
“ “ “ “ “	“ “ “ “ “	129	129	35	104	91	25	0.30	
“ “ “ “ “	Slag C . . . . .	137	124	33	101	90	31	0.31	
“ “ “ “ “	“ “ “ “ “	125	117	31	111	98	20	0.33	
“ “ “ “ “	Slag D . . . . .	117	105	29	111	88	26	0.30	
“ “ “ “ “	“ “ “ “ “	135	87	24	101	89	22	0.34	
“ “ “ “ “	Acid phosphate . . . . .	127	96	23	106	83	24	0.31	
“ “ “ “ “	“ “ “ “ “	132	..	..	..	..	..	..	
“ “ “ “ “	Double superphosphate . . . . .	119	118	45	108	102	22	0.34	
“ “ “ “ “	“ “ “ “ “	115	111	42	104	102	41	0.37	
“ “ “ “ “	Rock phosphate . . . . .	21	14	8	32	36	12	0.10	
“ “ “ “ “	“ “ “ “ “	21	49	17	37	27	8	0.08	
“ “ “ “ “	Sodium phosphate . . . . .	133	118	49	110	101	26	0.33	
“ “ “ “ “	“ “ “ “ “	122	98	14	96	102	19	0.38	
N P K Lx . . . . .	Sodium phosphate . . . . .	142	100	25	112	92	27	....	
“ “ “ “ “	“ “ “ “ “	151	121	37	103	99	31	....	
N 1 ½ P K 1 ½ L . . . . .	Sodium phosphate . . . . .	136	126	41	100	98	29	....	
“ “ “ “ “	“ “ “ “ “	..	..	..	..	..	..	....	
N P 1 ½ K L . . . . .	Sodium phosphate . . . . .	131	137	37	116	117	26	....	
“ “ “ “ “	“ “ “ “ “	149	140	35	109	114	27	....	
N P 2 K L . . . . .	Rock phosphate . . . . .	68	75	21	42	35	11	0.09	
“ “ “ “ “	“ “ “ “ “	36	72	18	37	38	8	0.09	

TABLE 19.

*Rhode Island Agricultural Experiment Station, 1915 and 1916. Field Experiment.*  
(Phosphates applied in 1915; none in 1916. Figures represent green weights in pounds per 1/80 acre.  
Crop: Dwarf Essex Rape)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	PLOT SERIES A YIELD IN GREEN WEIGHTS			PLOT SERIES B YIELD IN GREEN WEIGHTS			AVERAGE OF BOTH SERIES FOR 1915 AND 1916
		1915	1916	Total Yield Both Years	1915	1916	Total Yield Both Years	
Nothing . . . . .	None . . . . .	78	46	124	47	34	81	103
N K L . . . . .	None . . . . .	377	275	652	355	199	554	603
N P ½ K L . . . . .	Slag A . . . . .	451	277	728	594	210	804	766
" . . . . .	Slag B . . . . .	460	310	770	567	216	783	777
" . . . . .	Slag C . . . . .	441	365	806	574	161	735	771
" . . . . .	Slag D . . . . .	433	309	742	476	196	672	707
" . . . . .	Acid phosphate . . . . .	501	314	815	613	244	857	836
" . . . . .	Sodium phosphate . . . . .	{480 427	{343 292	{823 719}	616	212	828	790
N P K L . . . . .	Slag A . . . . .	515	375	890	613	251	864	877
" . . . . .	Slag B . . . . .	481	290	771	634	289	923	847
" . . . . .	Slag C . . . . .	476	307	783	659	202	861	822
" . . . . .	Slag D . . . . .	497	286	783	661	181	842	813
" . . . . .	Slag E . . . . .	457	265	722	626	216	842	782
" . . . . .	Rock phosphate . . . . .	415	280	695	508	171	679	687
" . . . . .	Acid phosphate . . . . .	539	403	942	627	310	937	940
" . . . . .	Sodium phosphate . . . . .	523	346	869	{672 662	{239 167	{911 829}	870
N P K Lx . . . . .	Sodium phosphate . . . . .	513	353	866	673	202	875	871
N 1 ½ P K 1 ½ L . . . . .	Sodium phosphate . . . . .	611	389	1000	716	261	977	989
N P 2 K L . . . . .	Sodium phosphate . . . . .	567	573	1140	715	449	1164	1152

\*American slag known as Duplex AA Basic Phosphate, manufactured by the Tennessee Coal, Iron & Railroad Co., Birmingham, Alabama. It contained 18.33 per cent of total phosphoric acid.

## FIELD EXPERIMENT.

The soil was located on the Underwood Farm; it was level and uniform in appearance but had not been under cultivation for a number of years and was producing but a scant crop of pasture grasses. The soil was 6¼ inches deep, and when dried 94.3 per cent was found to be finer than 1 mm. The lime requirement, according to the Veitch method, was 2073 pounds of calcium oxide per acre. The plots were laid out in accordance with the directions of the committee. Following the application of lime and the non-phosphatic fertilizers in the spring of 1912, a crop of oats, followed by buckwheat, was grown, followed by silage corn in 1913. In preparation for the latter crop, both nitrogen and potash were added. In 1914, finely ground limestone was added to all except the nothing plots and plot C at the rate of 1½ tons per acre. In early May the cover crop of crimson clover was plowed under, the non-phosphatic fertilizers added to furnish 80 pounds of nitrogen and 150 pounds of potash per acre, and on May 20 corn was planted. The average production of green silage corn where no phosphorus was added

TABLE 20.

*Rhode Island Agricultural Experiment Station, 1915 and 1916. Field Experiment.*

(Phosphates applied in 1915; none in 1916. Figures represent green weights in pounds per 1/80 acre. Crop: Japanese Millet.)

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	PLOT SERIES A YIELD IN GREEN WEIGHTS			PLOT SERIES B YIELD IN GREEN WEIGHTS			AVERAGE OF BOTH SERIES FOR 1915 AND 1916
		1915	1916	Total Yield Both Years	1915	1916	Total Yield Both Years	
Nothing . . . . .	None . . . . .	166	74	240	148	69	217	229
N K L . . . . .	None . . . . .	376	121	497	296	70	366	432
N P $\frac{1}{2}$ K L . . . . .	Slag A . . . . .	386	131	517	376	94	470	494
" . . . . .	Slag B . . . . .	435	151	586	361	79	440	513
" . . . . .	Slag C . . . . .	403	123	526	390	152	542	534
" . . . . .	Slag D . . . . .	406	121	527	395	176	571	549
" . . . . .	Acid phosphate . . . . .	403	120	523	353	75	428	476
" . . . . .	Sodium phosphate . . . . .	422	119	541	431	93	524	561
" . . . . .	" . . . . .	428	190	618	" . . . . .	" . . . . .	" . . . . .	" . . . . .
N P K L . . . . .	Slag A . . . . .	397	177	574	401	122	523	549
" . . . . .	Slag B . . . . .	378	158	536	411	113	524	530
" . . . . .	Slag C . . . . .	411	164	575	411	127	538	557
" . . . . .	Slag D . . . . .	417	174	591	408	112	520	556
" . . . . .	Slag E . . . . .	394	130	524	367	95	462	493
" . . . . .	Rock phosphate . . . . .	358	158	516	340	132	472	494
" . . . . .	Acid phosphate . . . . .	434	186	620	527	155	682	651
" . . . . .	Sodium phosphate . . . . .	467	170	637	408	122	530	555
" . . . . .	" . . . . .	" . . . . .	" . . . . .	" . . . . .	418	80	498	" . . . . .
N P K Lx . . . . .	" . . . . .	447	145	592	409	84	493	543
" . . . . .	Acid phosphate . . . . .	428	131	559	" . . . . .	" . . . . .	" . . . . .	" . . . . .
" . . . . .	" . . . . .	414	147	561	" . . . . .	" . . . . .	" . . . . .	" . . . . .
N P 2 K Lx . . . . .	" . . . . .	453	231	684	" . . . . .	" . . . . .	" . . . . .	" . . . . .
" . . . . .	" . . . . .	457	237	694	" . . . . .	" . . . . .	" . . . . .	" . . . . .
N P 2 K . . . . .	" . . . . .	409	261	670	" . . . . .	" . . . . .	" . . . . .	" . . . . .
N 1 $\frac{1}{2}$ P K 1 $\frac{1}{2}$ L . . . . .	Sodium phosphate . . . . .	452	159	611	450	154	604	608
N P 2 K L . . . . .	" . . . . .	462	229	691	487	204	691	691

was about 20 tons per acre. This did not indicate as great a deficiency of phosphorus as was desirable, yet it seemed best to start the experiment the following year.

*Season of 1915.*—Lime and fertilizer were applied to the plowed field on March 31 in the following amounts per acre: nitrate of soda, 200 pounds; dried blood, 600 pounds; high-grade sulfate of potash, 500 pounds; ground limestone, 1000 pounds. For the rape, 80 pounds, and for the millet, 60 pounds, per acre of  $P_2O_5$  were used for P. The rape was planted May 7 and harvested July 28; the millet was planted May 10 and 11, and harvested August 20. In early October the land was plowed, fitted, and sown to winter rye.

*Season of 1916.*—The fields received no phosphatic fertilizers in 1916, but did receive the following nitrogen and potash products, per acre: nitrate of soda, 250 pounds; ammonium sulfate, 200 pounds; dried blood, 500 pounds; muriate of potash, 100 pounds; common salt,

150 pounds. The extra lime plots received ground limestone at the rate of 1 ton per acre; the other plots received no additional lime. The rape field was planted May 3 and harvested August 24. The millet plots were planted May 25 and harvested September 8, 1916. A discussion of the results by Hartwell will be found in Bulletin 171, June, 1917, Rhode Island Agricultural Experiment Station. Table 19 shows the yields.

#### TEXAS AGRICULTURAL EXPERIMENT STATION.

Pot experiments were run on seven different soils. Each pot contained 5000 grams of soil and a quantity of phosphoric acid equal to 0.035 gram on the basis of total phosphoric acid in case of the slags and the phosphate rock, and available phosphoric acid in the acid phosphate.

#### DISCUSSION.

In making up the summary table of the pot experiments, which shows the average standing of each phosphate, both from the standpoint of increase in yield of crop and in phosphoric acid recovered, over the no-phosphate pots, the results of certain experiments have been purposely omitted—namely, wherever a small margin existed between the yields of the no-phosphate and the phosphate pots, indicating that the soil was not properly depleted in phosphorus prior to conducting the final experiment; and whenever serious damage resulted from the effects of insects or other pests. Footnotes following the tables giving the yields obtained in the various experiments show those cases where the exclusion of results from the summary tables seemed justified.

In the discussion of results of the pot experiments, as shown by the summary, Table 26, it might be pointed out that the closely agreeing results, both in crop yield and in phosphoric acid recovered, obtained by sodium phosphate N P K L, as compared with sodium phosphate N P K Lx (extra lime), indicate that the results were not vitiated by the lack of lime. Because the lime requirement of the soils was suitably provided for, it is reasonable to conclude that any extra lime that the slags may have supplied did not contribute to an increased yield on the slag pots. It is quite as apparent from a study of the table that neither nitrogen nor potash was a limiting factor in the experiment, for when these elements were supplied in quantities above the optimum, as in case of N 1  $\frac{1}{2}$  P K 1  $\frac{1}{2}$  L, a depressing or unfavorable condition was developed, as evidenced by the decreased yield.

It appears that the phosphorus was the greatest, and perhaps the only limiting factor, and a comparison of results obtained on the various phosphates indicates that conditions existed whereby the phosphate was enabled to exert its full effect, particularly when the smallest amounts of phosphoric acid were added.

TABLE  
*Texas Agricultural Experiment*  
 Crops: Corn,

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	SOIL No. 6884.					
		WEIGHT OF AIR-DRIED CROP AND $P_2O_5$ RECOVERED					
		Corn		Sorghum		Rye	
		Crop	$P_2O_5$	Crop	$P_2O_5$	Crop	$P_2O_5$
		grams	grams	grams	grams	grams	grams
N K L . . .	None . . . . .			14	0.018	6	0.009
" " . . .	" . . . . .	12	0.018	13	0.020	7	0.027
N P K L . .	Slag A . . .	24	0.019	15	0.020	4	0.009
" " . . .	Slag B . . .	18	0.021	17	0.026	6	0.011
" " . . .	" " . . . . .	23	0.029	19	0.027	7	0.011
" " . . .	Slag C . . .	24	0.027	10	0.015		
" " . . .	Slag D . . .	14	0.019	14	0.021	6	0.012
" " . . .	Acid phosphate	25	0.028	14	0.019	6	0.011
" " . . .	" " . . . . .	24	0.031	18	0.026	6	0.010
" " . . .	Rock phosphate	17	0.022	14	0.027	8	0.014
N P 2 K L	Acid phosphate	27	0.044	24	0.025	8	0.014

\*Only two crops.

NOTE.—The results on Soil No. 6884 are not used in the summary table as the small difference in yields between the phosphate and no-phosphate pots indicates that the soil was not properly depleted of phosphorus before the experiment was run. The results on Soil No. 6681 are included in the summary table.

With reference to a comparison of results obtained by the various slags, a consistently low yield is not found with any one of them. Under fallow conditions with the minimum application of phosphoric acid Slag C, with the lowest crop yield, stands only three points below Slag A, and only eight points below Slag D, which gave the highest yield. In the recovery of phosphoric acid, it is found that although Slag C is still at the bottom of the list, Slag D is a close second, Slag A standing third, and Slag B at the head.

Following legume turned under, with the minimum amount of phosphoric acid, it is found that in yield of crop Slag D, which was highest in the fallow series, stands lowest, followed by Slag A. Slags B and C gave the same availability in this series, being only nine points higher than Slag D. In the recovery of phosphoric acid, Slag D is still at the bottom of the list, followed by C, B, and A, in the order named.

About the same variation exists in the standing of the four slags where the medium amount of phosphoric acid was used. The variations noted are not on the whole greater than could be expected and accounted for through seasonal conditions and experimental error. The average standing of the four slags is, therefore, used in making a comparison with acid phosphate.

The average standing of the four slags in the vegetation pot work with the medium and smaller applications of phosphoric acid, on the

21.

*Station, 1914. Pot Experiment.**Sorghum, and Rye.*

SOIL No. 6681.						TOTAL WEIGHT OF THE THREE CROPS		TOTAL P <sub>2</sub> O <sub>5</sub> RECOVERED FROM THE THREE CROPS	
WEIGHT OF AIR-DRIED CROP AND P <sub>2</sub> O <sub>5</sub> RECOVERED									
Corn		Sorghum		Rye					
Crop	P <sub>2</sub> O <sub>5</sub>	Crop	P <sub>2</sub> O <sub>5</sub>	Crop	P <sub>2</sub> O <sub>5</sub>	Soil No. 6684	Soil No. 6681	Soil No. 6684	Soil No. 6681
<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
3	0.006	6	0.009	4	0.007	32	13	0.055	0.022
4	0.008	5	0.010	5	0.008	.	14	.	0.026
4	0.007	11	0.018	7	0.012	43	22	0.048	0.037
3	0.005	11	0.017	7	0.011	.	21	.	0.033
3	0.006	11	0.019	8	0.012	41	22	0.058	0.037
4	0.010	7	0.012	8	0.014	49	19	0.067	0.036
6	0.009	12	0.021	8	0.012	34 <sup>a</sup>	26	0.042 <sup>a</sup>	0.042
4	0.009	10	0.016	5	0.008	34	19	0.052	0.033
11	0.018	11	0.019	5	0.009	45	27	0.058	0.046
11	0.019	11	0.023	4	0.007	48	26	0.067	0.049
4	0.010	6	0.011	6	0.011	39	16	0.063	0.032
17	0.024	16	0.027	9	0.016	59	42	0.083	0.067

basis of crop yield, acid phosphate at 100, is 91; on the basis of phosphoric acid recovered, it is 106. Attention should here be called to results of chemical analyses of the four slags as contained in the report of the Committee on Availability of Phosphoric Acid in Basic Slag<sup>1</sup>. The available phosphoric acid in the slags was determined by the Wagner two per cent citric acid method. The average phosphoric acid availability on the four slags by this method was 91 per cent, which is exactly the same figure that represents the average standing of the four slags on the basis of crop yield, acid phosphate at 100, in the vegetation pot work.

Both the yield of crop and the phosphoric acid recovered with sodium phosphate used in the small, medium, and large amounts, showed a satisfactory gain over the other and less soluble phosphates, the average with the use of the small and medium amounts of phosphoric acid being in crop yield 118, and in phosphoric acid recovered 143, as compared with acid phosphate at 100.

The yields with double superphosphate closely paralleled the yields with acid phosphate, being 109 in crop yield and 96 in phosphoric acid recovered, as compared with acid phosphate at 100.

The yields with phosphate rock were consistently low, being in crop yield 20, and in phosphoric acid recovered 8, compared with acid phosphate at 100.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1915, 1: 102.

TABLE 22.  
*Texas Agricultural Experiment Station, 1914. Pot Experiment.*  
*Soil No. 6885.*

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	WEIGHT OF AIR-DRIED CROP AND P <sub>2</sub> O <sub>5</sub> RECOVERED						TOTAL WEIGHT OF THE THREE CROPS	TOTAL P <sub>2</sub> O <sub>5</sub> RECOVERED FROM THE THREE CROPS
		Corn		Sorghum		Rye			
		Crop	P <sub>2</sub> O <sub>5</sub>	Crop	P <sub>2</sub> O <sub>5</sub>	Crop	P <sub>2</sub> O <sub>5</sub>		
		<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
N K L ..	None .....	12	0.019	10	0.013	3	0.005	25	0.037
N P K L..	Slag A .....	17	0.030	19	0.025	5	0.008	41	0.063
“ ..	Slag B .....	20	0.036	25	0.028	10	0.015	55	0.079
“ ..	Slag C .....	13	0.019	17	0.023	6	0.010	36	0.052
“ ..	Acid phosphate.	24	0.038	14	0.019	4	0.008	42	0.065

*Soil No. 7230.*

N K L....	None .....	15	0.024	17	0.022	6	0.010	38	0.056
" ..	" .....	10	0.024	15	0.023	6	0.010	31	0.057
N P K L..	Slag A .....	23	0.041	19	0.033	7	0.012	49	0.086
" ..	" .....	16	0.036	20	0.029	9	0.015	45	0.080
" ..	Slag B .....	20	0.037	25	0.035	8	0.013	53	0.085
" ..	" .....	18	0.039	20	0.029	10	0.016	48	0.084
" ..	Slag C .....	19	0.026	23	0.030	8	0.013	50	0.069
" ..	Slag D .....	18	0.034	18	0.023	7	0.011	43	0.068
" ..	Acid phosphate...	25	0.045	22	0.031	7	0.011	54	0.087
" ..	" .....	24	0.050	23	0.033	8	0.013	55	0.096
" ..	Rock phosphate..	16	0.032	22	0.035	6	0.011	44	0.078
N P 2 K L	Acid phosphate..	29	0.060	25	0.039	11	0.017	65	0.116

*Soil No. 7236\*.*

N K L	None .....	7	0.013	12	0.017	6	0.013	25	0.043
" ..	" .....	5	0.012	8	0.013	4	0.005	17	0.030
N P K L..	Slag B .....	10	0.020	16	0.022	4	0.007	30	0.049
" ..	Slag C .....	2	0.006	12	0.020	5	0.009	19	0.035
" ..	Slag D .....	2	0.006	12	0.018	6	0.012	20	0.036
" ..	" .....	4	0.011	9	0.015	7	0.011	20	0.037
" ..	Acid phosphate...	10	0.021	15	0.021	4	0.007	29	0.049
" ..	Rock phosphate..	4	0.009	8	0.013	4	0.008	16	0.030
N P 2 K L	Acid phosphate..	17	0.028	18	0.029	4	0.011	39	0.068

\*These results are not used in the summary tables as the small difference in yields between the phosphate and no-phosphate pots indicates that the soil was not properly depleted of phosphorus before the experiment was run.

Owing to the unsatisfactory conditions that usually existed in the field experiments, no attempt is here made to summarize the results, which are, however, included in the preceding pages. The Rhode Island field experiment, which was the most satisfactory, showed in a comparison based on the increase in yield of crop over no-phosphate plot, acid phosphate in the smaller application at 100, an average standing of the slags of 88 with the smaller application of phosphate and 128 with the larger.

TABLE 23.  
*Texas Agricultural Experiment Station, 1915. Pot Experiment.*  
 Crops: Corn and Sorghum.  
 Soil No. 9283.

Soil No. 9285.

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	WEIGHT OF AIR-DRIED CROP AND P <sub>2</sub> O <sub>5</sub> RECOVERED				TOTAL WEIGHT OF THE TWO CROPS	TOTAL P <sub>2</sub> O <sub>5</sub> RECOVERED FROM THE TWO CROPS
		Corn		Sorghum			
		Crop	P <sub>2</sub> O <sub>5</sub>	Crop	P <sub>2</sub> O <sub>5</sub>		
		grams	grams	grams	grams	grams	grams
N K L . . .	None . . . .	9	0.024	9	0.014	18	0.038
" " " "	" " " "	8	0.023	9	0.015	17	0.038
N P K L . .	Slag A . . . .	12	0.029	12	0.023	24	0.052
" " " "	Slag B . . . .	10	0.029	12	0.022	22	0.051
" " " "	Slag C . . . .	13	0.033	10	0.019	23	0.052
" " " "	Slag D . . . .	10	0.029	10	0.019	20	0.048
" " " "	Acid phosphate	12	0.033	10	0.020	22	0.053
" " " "	Rock phosphate	7	0.021	9	0.020	16	0.041

Soil No. 9288.

N K L . .	None . . . .	9	0.011	1	0.004	10	0.015
" " " "	" " " "	7	0.011	1	0.003	8	0.014
N P K L . .	Slag A . . . .	11	0.020	4	0.009	15	0.029
" " " "	Slag B . . . .	12	0.018	2	0.006	14	0.024
" " " "	Slag C . . . .	10	0.015	1	0.003	11	0.018
" " " "	Slag D . . . .	8	0.015	2	0.003	10	0.018
" " " "	Acid phosphate	11	0.015	2	0.005	13	0.020
" " " "	Rock phosphate	8	0.013	2	0.003	10	0.016

TABLE 24.  
*Summary of Results of Pot Experiments.*

FORMULA TREATMENT	SOURCE OF PHOSPHORIC ACID	AVERAGE STANDING OF EACH PHOSPHATE. BASIS, INCREASE IN YIELD OF CROP AND PHOS- PHORIC ACID RECOVERED OVER NO-PHOSPHATE POTS. ACID PHOSPHATE AT 100.			
		Fallow		Legume Turned Under	
		Crop	$P_2O_5$ Recovered	Crop	$P_2O_5$ Recovered
N K L . . . .	None . . . . .				
N P $\frac{1}{2}$ K L . .	Slag A . . . . .	79	97	88	127
" " " "	Slag B . . . . .	83	100	94	123
" " " "	Slag C . . . . .	76	83	94	113
" " " "	Slag D . . . . .	84	85	85	105
" " " "	Average, Slags A, B, C, D	81	91	90	117
" " " "	Acid phosphate . .	100	100	100	100
" " " "	Phosphate rock . . .	13	12	23	3
" " " "	Sodium phosphate . .	100	150	128	130
" " " "	Double superphosphate .	102	91	115	99
N P K L . . . .	Slag A . . . . .	109	112	88	127
" " " "	Slag B . . . . .	108	107	89	111
" " " "	Slag C . . . . .	103	105	90	102
" " " "	Slag D . . . . .	95	97	88	105
" " " "	Average, Slags A, B, C, D	104	105	89	111
" " " "	Acid phosphate . . . .	100	100	100	100
" " " "	Phosphate rock . . . .	21	7	22	8
" " " "	Sodium phosphate . . .	122	149	121	143
" " " "	Double superphosphate .	113	98	106	95
N P K L x . . . .	Sodium phosphate . . . .	128	142	122	144
N $1\frac{1}{2}$ P K $1\frac{1}{2}$ L	Sodium phosphate . . . .	95	24	89	43
N P $1\frac{1}{2}$ K L . . . .	Sodium phosphate . . . .	152	193	127	183
N P 2 K L . . . .	Phosphate rock . . . . .	43	22	32	24



## CONCLUSIONS.

The purpose of the vegetation experiments was to determine the availability of the phosphoric acid contained in Thomas-Bessemer basic slag phosphate, and to determine whether the Wagner method of analysis was a reliable procedure for measuring the availability of the phosphoric acid in this class of products.

The results obtained by the experiment have established the fact that all four slags contained their phosphoric acid in forms freely available to the crops grown, comparing favorably, both in yield of crop and in phosphoric acid recovered, with results obtained with acid phosphate. Moreover, the availability figures established by the vegetation pot work compare favorably with the available phosphoric acid as measured by the Wagner method for Thomas basic slag phosphate and the official neutral citrate of ammonia method for acid phosphate or superphosphates.

H. D. HASKINS,  
J. A. BIZZELL,  
W. B. ELLETT,

B. L. HARTWELL,  
C. B. WILLIAMS.

*Committee on Vegetation Tests on the Availability of Phosphoric Acid in Basic Slag.*

The committee feels that this report terminates a splendid piece of cooperative work, which aptly illustrates the commendable spirit of earnestness and patience that prevails among the members of the Association of Official Agricultural Chemists. The association and the world at large are greatly indebted to the contributors for their careful and painstaking efforts.

REPORT OF THE COMMITTEE TO COOPERATE WITH THE  
AMERICAN SOCIETY FOR TESTING MATERIALS  
ON THE SUBJECT OF AGRICULTURAL LIME.

This committee made a report to the association at its last meeting<sup>1</sup>. At that time progress was reported in the conferences with Committee C-7 of the American Society for Testing Materials, through its two sub-committees, IV—Agricultural Lime and V—Methods of Analysis, as follows: "It was agreed that uniformity in the methods of the two bodies would prove desirable. It was further agreed, however, that precision requirements are not identical for liming materials for industry and agriculture".

The committee was continued and directed to prepare a chapter on "Liming Materials" for insertion in "Methods of Analysis". It has

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 255.

done this work and attaches herewith the proposed methods as part of the report. Where applicable tentative or official methods already described in "Methods of Analysis" were used; they are indicated by cross-references.

The methods offered are advanced after careful study of the procedures compiled by the A. S. T. M. Those procedures, drawn with intent to furnish control methods in business contracts for commercial lime, call for the determination of substances of no known agricultural value. Effective oxides, rather than impurities, determine the value of lime for soils. The methods here appended were compiled with this thought in mind.

### **AGRICULTURAL LIMING MATERIALS—TENTATIVE.**

#### **1**

##### **DIRECTIONS FOR SAMPLING.**

The sample shall be representative of the lot or shipment and shall not contain a disproportionate quantity of the surface or of any modified or damaged zone.

#### **2**

##### **BURNT, LUMP LIME, IN BULK.**

Collect a composite sample by taking not less than ten shovelfuls, each from a different part of the shipment. Immediately crush the whole sample to pass a 1-inch ring; mix thoroughly and rapidly; quarter down to a 5-pound sample; and place in a properly labeled, dry, air-tight container.

#### **3**

##### **BURNT, LUMP LIME, IN BARRELS.**

Sample at least 5 barrels, selected at random from each car, and handle as directed for burnt, lump lime, in bulk (2).

#### **4**

##### **HYDRATED LIME, GROUND BURNT LIME, IN BAGS.**

By means of a slotted sampling tube, withdraw a sample the full depth of each of 10 bags, selected from different points in the car; immediately mix thoroughly on a clean cloth and place a sufficient sample in a properly labeled, dry, air-tight container.

#### **5**

##### **GROUND LIMESTONE, GROUND MARL, IN BAGS.**

Proceed as prescribed for hydrated lime in bags (4).

#### **6**

##### **GROUND LIMESTONE, GROUND BURNT LIME, GROUND MARL, IN BULK.**

By means of a slotted sampling tube, withdraw samples full sampler depth from 10 points in the car; mix thoroughly; and from this composite withdraw a sample and place in a properly labeled, dry, air-tight container.

#### **7**

##### **PREPARATION OF SAMPLE.**

Grind the sample with a porcelain mortar and pestle or in a porcelain ball mill to pass a 60-mesh sieve, mix thoroughly, quarter, and preserve in an air-tight container.

#### **8**

##### **TOTAL ALKALINITY.**

Place 0.5 gram of burnt or hydrated lime (1 gram of ground limestone or ground marl), prepared as directed in 7, in a 150 cc. beaker; add 50 cc. of 0.5N nitric acid, cover beaker with watch glass, and boil for 5 minutes. Cool, titrate excess of acid with 0.5N or 0.25N alkali, using phenolphthalein, and calculate results as percentage of calcium oxide.

## 9

## CALCIUM OXIDE IN BURNT AND HYDRATED LIME.

*Stone and Scheuch method<sup>1</sup> as modified by MacIntire and Shaw<sup>2</sup>.*

Boil 250 cc. of distilled water for 2 minutes and dissolve in it 25 grams of pure cane sugar. Place 1.4 grams of material, prepared as directed in 7, in a 500 cc. graduated flask; add 25 cc. of freshly boiled hot water; stopper flask; and agitate for 1 minute. Run in the hot aqueous sugar solution and boil for 20 minutes. Cool under tap, make to volume with carbon-dioxide-free distilled water, and agitate vigorously for 5 minutes. Filter about 125 cc. through a dry filter on a 9 cm. Büchner funnel leading into a small beaker placed under a bell jar. Cover the funnel with a watch glass and titrate 100 cc. of this filtrate with 0.25N hydrochloric acid. Deliver about 1 cc. less than 2.5 times the 0.25N acid required in this preliminary titration into a 400 cc. beaker. Place a flask, calibrated to deliver 250 cc., under the bell jar and filter 250 cc. of the lime-sucrose solution. Pour this 250 cc. into the 400 cc. beaker containing the 0.25N hydrochloric acid, add phenolphthalein, and complete titration. The number of cc. of 0.25 normal acid required is the percentage of calcium oxide present as oxide or hydrate.

## 10

*Proctor method<sup>3</sup>, as modified by Veitch and Jarrell<sup>4</sup>.*

Place 1 gram of the thoroughly mixed sample, prepared as directed in 7, in a graduated liter flask; add about 10 cc. of hot freshly boiled distilled water; and shake well. After the lime has slaked add about a dozen small glass beads and about 950 cc. of freshly boiled distilled water of room temperature, stopper, and shake six times for 5 minutes each at intervals of 1 hour. Fill to the mark, mix thoroughly, and allow to stand until practically clear, or overnight. Carefully pipet 100 cc. of the clear solution into an Erlenmeyer flask, add several drops of phenolphthalein solution, titrate at once with 0.1N hydrochloric acid, and calculate as available calcium oxide.

## 11

*Scaife method<sup>5</sup>.*

Place 1.4 grams of the thoroughly mixed sample, prepared as directed in 7, in a 250 cc. beaker; add about 150 cc. of hot water; cover the beaker; heat carefully; and boil for 3 minutes. Cool, wash down the cover, add 2 drops of phenolphthalein, and titrate with normal hydrochloric acid, adding the acid as rapidly as possible by dropping, and stirring vigorously to avoid local excess of acid. When white spots appear, add the acid more slowly, but continue until the pink color fades out throughout the solution for a second or two. Note the amount of acid used and ignore the return of color. Repeat the experiment, using a 500 cc. graduated flask instead of a beaker, and add 5 cc. less normal acid than before. Designate the number of cc. used as "A". Grind up any small lumps with a glass rod slightly flattened at one end, dilute to the mark with distilled water, mix thoroughly for 5 minutes, and let settle for one-half hour. Draw off 100 cc. of the solution without filtering, add phenolphthalein, and titrate with 0.5N hydrochloric acid. Designate this additional number of cc. as "B". The percentage of available  $\text{CaO} = 2A + 5B$ .

## 12

## CARBON DIOXIDE.

Determine, as directed under Soils 5 (a) or 5 (b)<sup>6</sup> or as directed under Baking Powders 5<sup>7</sup>, the carbon dioxide in 5 grams of burnt or hydrated lime (2 grams of ground limestone or ground marl), prepared as directed under 7. Calculate and express the results as the percentage of calcium carbonate.

<sup>1</sup> *J. Am. Chem. Soc.*, 1894, 16: 721.

<sup>2</sup> Procedure to be published soon.

<sup>3</sup> *Textbook of Tanning*, 1885, 102; *Principles of Leather Manufacture*, 1903, 125.

<sup>4</sup> *J. Am. Leather Chem. Assoc.*, 1921, 16: 440.

<sup>5</sup> *Concrete*, 1917, 10: 25; *J. Am. Leather Chem. Assoc.*, 1921, 16: 438-44; *Chem. Met. Eng.*, 1921, 25: 740.

<sup>6</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 310.

<sup>7</sup> *Ibid.*, 275.

## 13

## TOTAL CALCIUM AND MAGNESIUM OXIDES.

Place 1 gram of burnt or hydrated lime (2 grams of ground limestone or ground marl), prepared as directed in 7, in a hard glass, 250 cc. beaker; cover with 25 cc. of water; add 10 cc. of hydrochloric acid and a few drops of nitric acid; boil 10 minutes; and evaporate to dryness. From this solution separate and remove silica, insoluble matter, iron and aluminium oxides as directed under Soils 14 and 15<sup>1</sup>; determine calcium oxide as directed under 16<sup>1</sup> and magnesium oxide as directed under 17<sup>2</sup>, Soils, using three times the quantity of ammonium phosphate solution there specified.

## 14

## MECHANICAL ANALYSIS OF GROUND LIMESTONES.

Transfer 100 grams of the original material to a set of 10, 20, 40, 60, 80, and 100 mesh Bureau of Standard sieves. Sift, shaking for 5 minutes on the 80 and 100 mesh sieves and breaking up the lumps by means of a soft rubber pestle if the material has a tendency to ball. Weigh the material that is retained on each sieve and that which passes the 100 mesh sieve, and express as percentage.

It is recommended—

(1) That the methods as compiled by this committee be inserted as a chapter, entitled "Agricultural Liming Materials—Tentative", in the "Methods of Analysis" of the association.

(2) That the methods for calcium oxide in burnt and hydrated limes be subjected to further study.

W. H. MACINTIRE,      J. B. WEEMS.  
F. P. VEITCH,

*Committee to Cooperate with the American  
Society for Testing Materials on the  
Subject of Agricultural Lime.*

Approved.

It was moved, seconded, and voted that the report of this committee be received and that the committee be discharged with the thanks of the association.

The report of the Committee on Revision of Methods of Soil Analysis will be published in the next number of *The Journal*, Vol. VII, No. 4.

<sup>1</sup> *Assoc. Official Agr. Chemists*, 1920, 315.

<sup>2</sup> *Ibid.*, 316.

REPORT OF COMMITTEE ON RECOMMENDATIONS  
OF REFEREES.

By R. E. DOOLITTLE (Food and Drug Inspection  
Station, Chicago, Ill.), *Chairman*.

The principal work of the Committee on Recommendations of Referees has been presented to the association in the reports of Sub-committees A, B, and C on the recommendations of referees and associate referees. As usual, a considerable number of referees' reports were not received until a few days before the meeting—in fact a number did not reach the chairman of the committee until the first and second days of the meeting. Proper consideration of referees' recommendations can not be given under such conditions. Sub-committees A, B, and C are required to consider the reports of about sixty referees and associate referees, in which consideration not only must the report of the work of the past year be reviewed but recommendations made must be viewed in the light of previous work on the same and similar subjects. This can not be done in the thorough and comprehensive manner deserved when the reports are not in the hands of the committee until the day of the meeting. Apparently, there were a greater number of delayed reports this year than usual. It is the opinion of the committee that some action will have to be taken to insure the submission of reports at a date sufficiently in advance of the meeting as to enable Sub-committees A, B, and C not only to study the reports but to give opportunity to take up with the referees by correspondence questions arising from recommendations made. Probably this can be accomplished best by fixing a date after which no reports will be considered until the following year. This may shorten the program considerably for the next meeting, but after the first year it should make little difference. If such a rule had been in effect this year not more than one-half of the referees' reports could have been considered.

The committee, in addition to the consideration of reports of referees, has given attention to the matter of organization of the work of the referees and associate referees to the end that there may be less duplication in their studies, better coordination of their plans, and greater continuity of their work until a conclusion is reached. It appears from inquiries made that in some instances referees and associate referees have taken up their work without giving consideration to the recommendations made or work done by former referees; that sometimes the retiring referee has made no recommendations concerning further work and the new referee has been in doubt as to what was the most important problem for him to take up; while in others the referee has felt that he was restricted in his activities to the carrying out of

the recommendations of the former referee, although these were not in accord with his own opinion as to what was the problem of most pressing importance in the field he was supposed to cover.

As the referee work is now carried on no method is provided whereby the Committee on Recommendations of Referees, the Executive Committee, the Secretary, or other official is notified of plans formulated for or progress made in the work during the year. The first and only information the Committee on Recommendations of Referees receives concerning the type of work engaged in by a referee is usually his report, which comes to hand a few days before the annual meeting. Failure to receive a report is often the first intimation the committee has that a referee has not been active during the year. The situation was discussed with the Executive Committee at its meeting in Washington on November 17th, with the result that certain suggestions were formulated for securing a better coordination of the work of the referees and associate referees with the needs of the association. These are as follows:

It is proposed that the work of the referees and associate referees shall be organized on what may be designated, in absence of a better term, as a project basis—that is a definite plan of operation whereby the work of these officials shall be carefully determined in advance after consideration of all information and data from previous work done, existing methods, and the work of other referees, and having once been determined upon shall be carried through to a definite conclusion. To effect this it is proposed (1) that all work on a product or a group of similar products, which is usually a chapter in the *Book of Methods*, shall be assembled under the leadership of one referee to be known as a general, or group, referee, and that each line of work under that subject shall be placed in the hands of an associate referee; (2) that each associate referee immediately upon receipt of notice of appointment shall prepare and submit to the general referee an outline of the work he proposes to do during the year, this plan to be based upon the recommendations approved by the association through the reports of Sub-committees A, B, and C; (3) that the general referee shall consider the plan proposed by the associate referee, particularly for proper coordination with the work of other associate referees on his subject and with existing methods and notify the associate referee of his approval of the plan submitted or the modifications deemed necessary. The general referee shall also notify the Chairman of the Committee on Recommendations of Referees of the final plans adopted by the associate referees on his subject. Similarly referees operating independently and not in groups under a general referee shall notify the Chairman of the Committee on Referees of their plans for work for the year. The Committee on Recommendations of Referees will endeavor to exercise the utmost

care in its consideration of recommendations for further work in order that incoming referees will not be bound to lines of studies that promise no profitable returns to the association. However, conditions frequently arise which greatly affect the importance of studies of methods, and where an incoming referee disagrees with the recommendations of the preceding referee as acted upon by the association and is of the opinion that a different line of work may be taken up to better advantage he shall consult with and secure the approval of the general referee before proceeding with a line of work not called for by existing recommendations. The general referee shall also, upon approval of the Executive Committee, have authority to appoint additional associate referees to undertake studies of pressing importance.

These suggestions were presented at a conference of the officials of the association, including the Executive Committee and incoming referees and associate referees, in so far as it was possible to notify them, in this room this morning. All comments received were favorable to the plan. Additional suggestions were made (1) that the associate referees shall make brief reports of the progress of their work quarterly to the general referee who in turn shall make a similar brief report to the Chairman of the Committee on Recommendations of Referees; and (2) that the final reports of referees and associate referees shall be in the hands of the Chairman of the Committee on Recommendations of Referees not later than September 1st (annual meeting to be held about middle of October), otherwise consideration will go over until another year.

The success of the project plan proposed depends to a great extent upon the close cooperation of the general referees and the associate referees to the end that there may be a proper coordination of work. Quarterly reports of progress would encourage such cooperation and be, therefore, very acceptable to the Committee on Recommendations of Referees. And certainly if Sub-committees A, B, and C are to give proper consideration to the recommendations of referees and associate referees, not only with reference to deletions, additions, and changes in methods, but also to further work, the reports must be in the hands of the chairmen of these committees several weeks prior to the annual meeting. Members of the association who have served on these committees well know the absolute necessity of consulting with referees and associate referees regarding recommendations made. If this can not be done personally sufficient time must be given for correspondence. The committee therefore approves the second suggestion made at the conference this morning.

The committee appreciates that this is a rather fragmentary presentation of the plan that is being worked out for coordinating the work of the referees and associate referees to carry out the objects of the association, but it will perhaps give some idea of what the committee

has in mind, namely, the organization of the referee work of the association on a definite project basis in the same manner as is the research work of the experimental stations, universities, colleges, and other scientific organizations with which the members of this association are connected.

## REPORT OF SUB-COMMITTEE A ON RECOMMENDATIONS OF REFEREES.

By W. H. MACINTIRE (University of Tennessee, Agricultural Experiment Station, Knoxville, Tenn.), *Chairman*.

[Water (including brines and salt), tanning materials and leather, insecticides and fungicides, soils (sulfur in soils), hydrogen-ion concentration in agricultural products, foods and feeding stuffs (crude fiber, starch in the presence of interfering polysaccharides, stock feed adulteration), saccharine products (honey, maple products, maltose products, sugar-house products), fertilizers (borax in fertilizers, preparation of ammonium citrate, nitrogen, potash), inorganic plant constituents (sulfur and phosphorus in seeds of plants; calcium, magnesium, iron, and aluminium in the ash of seeds).]

### WATER.

It is recommended—

(1) That the method for the determination of bromine in the presence of chlorine and iodine, as published in *The Journal*<sup>1</sup>, be adopted as a tentative method.

Approved.

(2) That the method for the determination of free and albuminoid ammonia in waters containing sulfide<sup>2</sup> be adopted as official. (Final action. First action was taken in 1919<sup>3</sup>.)

Approved.

(3) That the title of Chapter III of Methods of Analysis be changed from "Waters" to "Waters, Brine, and Salt". This recommendation is in accord with Recommendation 6<sup>3</sup>, submitted by the Referee on Water in 1919, "that the methods on water be extended to cover the examination of allied products, such as brine and salt".

Approved.

(4) That the methods for the examination of salt, as given in the report of the referee, be adopted as tentative methods.

Approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 29.

<sup>2</sup> *Ibid.*, 4, 387.

<sup>3</sup> *Ibid.*, 566.



- (5) That the methods for salt published previously<sup>1</sup> be dropped.  
Approved.

#### TANNING MATERIALS AND LEATHERS.

It is recommended—

- (1) That the revised methods for the analysis of tanning materials submitted by the referee be adopted by the association as tentative and substituted for the present tentative methods<sup>2</sup>.

Approved.

- (2) That the revised methods for the analysis of leathers, submitted by the referee, be adopted by the association as tentative and substituted for the present tentative methods<sup>3</sup>.

Approved.

- (3) That methods for the determination of tannin in tanning materials and leather be studied with a view to the working out of a more accurate method.

Approved.

- (4) That the study of solvents in the determination of grease, soap, and oxidized oils and fats in leather be continued.

Approved.

#### INSECTICIDES AND FUNGICIDES.

It is recommended—

- (1) That the hydrazine distillation method for the determination of total arsenic<sup>4</sup> be adopted as an official method. (Final action.)

Approved.

- (2) That the method for the determination of total arsenic in the presence of sulfides, sulfites, and thiosulfates, or large amounts of sulfur, as described in the referee's report, be adopted as a tentative method.

Approved.

*The following recommendations refer to revisions of the methods in the chapter on Insecticides and Fungicides, Methods of Analysis, 1920.*

It is recommended—

- (1) That the following methods be grouped under the heading "General Methods" and placed at the beginning of the chapter:

Preparation of the Sample; Moisture; Copper Chloride and Hydrazine Distillation Methods for Total Arsenic, including both iodine and bromate titrations; Water-soluble Arsenic; and the General Procedure for the Analysis of Products Containing Arsenic, Antimony, Lead, Copper, Zinc, Iron, Calcium, Magnesium, etc.

Approved.

- (2) That directions for the use of factor weights be discontinued,

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 384.

<sup>2</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 43.

<sup>3</sup> *Ibid.*, 49.

<sup>4</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 402.

and that statements of the approximate weights of sample to be used be incorporated in their stead.

Approved under suspension of the rules.

(3) That Paragraph 4, "Apparatus", be changed as described in the report of the referee.

Approved under suspension of the rules.

(4) That Paragraphs 7 and 8, Methods 1 and 2 for total arsenious oxide, be combined into one method, as described in the referee's report, and be adopted as an official method.

Approved for final action as an official method under suspension of the rules.

(5) That Paragraph 47, "Method I.—Tentative", for copper, be changed as described in the report of the referee and be adopted as an official method.

Approved.

(6) That Paragraphs 68 and 69, "Hydrogen Peroxide Method.—Official", for the determination of formaldehyde in formaldehyde solutions, be amended to permit the use of brom-thymol blue as an optional indicator.

Approved for final action under suspension of the rules.

(7) That Paragraph 81, "Sulfate Sulfur.—Official", be changed as described in the report of the referee.

Approved for final action under suspension of the rules.

(8) That the following tentative methods be adopted as official methods:

Paragraph 1.—Preparation of Sample.

Paragraph 2.—Moisture in Paris Green.

Paragraphs 11 and 12.—Water-soluble Arsenious Oxide in Paris Green.

Paragraph 15.—Moisture in London Purple.

Paragraph 20.—Water-soluble Arsenious Oxide in London Purple.

Paragraphs 21 and 22.—Water-soluble Arsenic Oxide in London Purple.

Paragraph 23.—Moisture in Lead Arsenate.

Paragraphs 25 and 26.—Total Lead Oxide in Lead Arsenate.

Paragraphs 30 and 31.—Water-soluble Arsenic in Lead Arsenate.

Paragraphs 32 and 33.—Total Arsenious Oxide in Lead Arsenate.

Paragraph 36 (f)<sup>1</sup>.—Total Arsenious Oxide in Magnesium Arsenate.

Paragraph 38.—Total Arsenious Oxide in Zinc Arsenite.

Paragraph 45.—Moisture in Bordeaux Mixture with Paris Green.

Paragraphs 50 and 51.—Total Arsenious Oxide in Bordeaux Mixture with Paris Green.

Paragraph 52.—Water-soluble Arsenious Oxide in Bordeaux Mixture with Paris Green.

Paragraph 58.—Water-soluble Arsenic in Bordeaux Mixture with Lead Arsenate.

Approved under suspension of the rules.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 4: 403; *Assoc. Official Agr. Chemists, Methods*, 1920, 59.

(9) That the following tentative methods be dropped:

Paragraph 15 (b).—Total Arsenic in London Purple.

Paragraph 36 (c).—Total Arsenious Oxide in Calcium Arsenate.

Paragraph 48.—Method II for Copper in Bordeaux Mixture with Paris Green.

Paragraph 55.—Copper in Bordeaux Mixture with Lead Arsenate.

Paragraph 56.—Lead Oxide in Bordeaux Mixture with Lead Arsenate.

Approved under suspension of the rules.

The committee also recommends that the paper by R. C. Roark, and that by C. C. Hedges and W. A. Stone be referred to the incoming referee.

Approved.

#### SOILS.

It is recommended—

(1) That the methods for the analysis of soils, as revised by the Committee on Revision of Methods of Soil Analysis and edited by the Committee on Editing Methods of Analysis, be adopted as tentative methods and substituted for the present tentative methods for Soils<sup>1</sup>.

Approved.

(2) That the methods for the analysis of liming materials, compiled by the Committee to Cooperate with the American Society for Testing Materials on the Subject of Agricultural Lime, be adopted as tentative and included as a separate chapter in the Revised Methods of Analysis.

Approved.

(3) That an associate referee be appointed to study ratios of soil to water in the determination of pH values.

Approved.

#### SULFUR IN SOILS.

It is recommended—

(1) That the method of Shaw and MacIntire<sup>2</sup> for the determination of total sulfur in soils be adopted as a tentative method and referred to the Committee on Revision of Methods of Soil Analysis for incorporation in the revised chapter of methods for soils.

Approved.

#### DETERMINATION OF ACTIVE ACIDITY OR HYDROGEN-ION CONCENTRATION FOR AGRICULTURAL PRODUCTS.

No report or recommendations.

#### FOODS AND FEEDING STUFFS.

It is recommended—

(1) That the comparative study of the official and C. R. Smith methods for the determination of ether extract be discontinued.

Approved.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 309.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1923, 15, 1183.

(2) That no further study be made of the effect of fineness of grinding upon the determination of ether extract.

Approved.

(3) That the incoming referee study the official methods for the determination of water in foods and feeding stuffs, with a view to rewording and fixing rigidly the conditions of temperature, pressure, and other factors.

Approved.

(4) That a method suitable for the determination of water in dried food be sought and submitted to the association.

Approved.

#### CRUDE FIBER.

It is recommended—

(1) That the method for the determination of crude fiber as given in the report of the referee be adopted as official and substituted for the method adopted at the 1921 meeting<sup>1</sup>. (First action as an official method.)

Approved.

(2) That the modification for the determination of crude fiber in prepared mustard<sup>2</sup> and similar seed materials be referred to the Referee on Spices and Other Condiments for consideration.

Approved.

#### STARCH IN THE PRESENCE OF INTERFERING POLYSACCHARIDES.

It is recommended—

(1) That further study be made of the method for the determination of starch in the presence of interfering polysaccharides<sup>3</sup>, attention being given to a more complete precipitation of the polysaccharides, to the advisability of employing the originally prescribed 300 cc. Erlenmeyer flask in order to obviate lumping, and to a comparison with other methods.

Approved.

#### STOCK FEED ADULTERATION.

It is recommended—

(1) That further study of the method for the determination of added oat hulls, investigated by the referee last year, be discontinued.

Approved.

(2) That the method submitted by the referee for the detection of added salt be subjected to further collaborative study, in which is included a wider range of products.

Approved.

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 421.

<sup>2</sup> *Ibid.*, 1923, 6: 344.

<sup>3</sup> *Ibid.*, 351.

## SACCHARINE PRODUCTS.

## HONEY.

It is recommended—

(1) That further study be made of the resorcin and aniline chloride tests<sup>1</sup> for the detection of added invert sugar.

Approved.

(2) That the recommendation of the referee that the "Conclusions" be made a part of the official methods of analysis be referred to the incoming general and associate referees for consideration.

Approved.

## MALTOSE PRODUCTS.

It is recommended—

(1) That the work on maltose products be continued along the same lines as last year.

Approved.

## SUGAR-HOUSE PRODUCTS.

It is recommended—

(1) That in Method (1)<sup>2</sup> "Drying upon Pumice Stone.—Official", at 70°C. in vacuo, there be inserted as the second sentence the following: "Digest with dilute sulfuric acid (1 to 4) 8 hours on the steam bath; wash free of acid and heat to dull redness (about 425°)".

Approved.

(2) That Method (2), "Drying upon Quartz Sand.—Official", be revised so as to provide for the use of a larger proportion of sand to dry substance. (20 to 30 grams of sand to 1 gram of dry substance.)

Approved.

(3) That Method (2), including changes suggested by the referee for modifying the directions to include the analysis of materials containing substances like fructose, which decompose rapidly, be subjected to further collaborative study.

Approved.

(4) That collaborative work be continued with the newer methods and apparatus for the determination of solids by drying, namely, the Spencer oven, the Seidenberg gauze dish, and the Brown-Duvel moisture tester.

Approved.

(5) That in view of the errors in the densimetric<sup>3</sup> and refractometric<sup>4</sup> methods, collaborative work on these methods be continued.

Approved.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 112.

<sup>2</sup> *Ibid.*, 101.

<sup>3</sup> *Ibid.*, 102.

<sup>4</sup> *Ibid.*, 105.

(6) That the formulas<sup>1</sup> used in the determination of sucrose by polarization be studied.

Approved.

#### FERTILIZERS.

##### BORAX IN FERTILIZERS.

It is recommended—

(1) That the Ross-Deemer<sup>2</sup> method for water-soluble boric acid and the Bartlett<sup>3</sup> method for total boric acid be adopted as official. (Final action.)

Approved.

##### PREPARATION OF AMMONIUM CITRATE.

It is recommended—

That the Robinson procedure<sup>4</sup> for the preparation of ammonium citrate be adopted as official. (Final action.)

Approved.

##### NITROGEN.

It is recommended—

That the Devarda<sup>5</sup> and Moore<sup>6</sup> methods be further studied.

Approved.

##### POTASH.

No report or recommendations.

*The following recommendations refer to revisions of the methods in the chapter on Fertilizers, Methods of Analysis, 1920.*

It is recommended—

(1) That "Directions for Sampling.—Official" be inserted as a separate paragraph, and that the last sentence of the paragraph, "Pass the entire sample, etc.", be placed at the opening of the paragraph "Preparation of Sample.—Official".

Approved under suspension of the rules.

(2) That the following changes be made in Paragraph 5, "Preparation of Solution":

1. That methods (a), (d), and (f) be deleted, and the necessary changes in designations be made in lettering.

2. That the statement "or 250 cc. if a 2.5 gram sample was used" be deleted.

3. That to (a) now (b) add "suitable for organic materials like cotton-seed meal alone or in mixtures".

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 75.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 327.

<sup>3</sup> *Ibid.*, 1921, 5: 90.

<sup>4</sup> *Ibid.*, 96.

<sup>5</sup> *Ibid.*, 1922, 5: 451.

<sup>6</sup> *J. Ind. Eng. Chem.*, 1919, 12: 669.

<sup>7</sup> *J. Assoc. Official Agr. Chemists*, 1921, 4: 566.

4. That to (b) now (c) for "Kjeldhal flask" substitute "200 cc. flask" and add "Generally applicable to materials, or mixtures, containing large quantities of organic matter. With cottonseed meals and materials of like nature, it is best to add about 5 cc. of concentrated nitric acid before the addition of the sulfuric acid, and allow to digest, at a gentle heat, if necessary, until the violence of the reaction is over, before adding the nitrate".

5. That to (c) now (e) add, "Suitable for materials containing small quantities of organic matter".

Approved for first action of a change in an official method.

(3) That in Paragraph 6, "Determination", the phrase "Nearly neutralize with hydrochloric acid" be deleted, and that "Neutralize the cooled solution with hydrochloric acid, using litmus as an indicator, and then add 1 cc. of concentrated hydrochloric acid" be substituted.

Approved under suspension of the rules.

(4) That Paragraph 8, "Preparation of Solution", be accordingly changed to read, "Dissolve according to 5 (b), (c), or (d), preferably by (c), when these acids are suitable solvents, and dilute to 200 cc. with water".

Approved for first action of a change in an official method.

(5) That in line 6, Paragraph 9 (a), "45-50°C." be substituted for "60-65°C."

Approved under suspension of the rules.

(6) That in line 9, Paragraph 9 (a) "Allow to remain in the bath, stirring occasionally for 30 minutes" be substituted for "Stir, let stand in the bath about 15 minutes".

Approved under suspension of the rules.

(7) That 9 (b) be deleted.

Approved under suspension of the rules.

(8) That 9 (c) be changed to 9 (b).

Approved under suspension of the rules.

(9) That after "shaking apparatus" 9 (c), there be inserted "or stirring apparatus" and after the word "shake" there be inserted the words "or stir".

Approved under suspension of the rules.

(10) That Paragraph 10, "Gravimetric Method.—Official", for the determination of water-soluble phosphoric acid, be prefaced by the sentence "If mechanical condition makes necessary, triturate 2 grams of the sample with a small amount of water and wash on filter. Otherwise place, etc."

Approved under suspension of the rules.

(11) That the Robinson procedure<sup>1</sup> for the preparation of ammonium

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 96.

citrate be inserted in Paragraph 12, page 4, with a statement that this method is to be preferred to either (1) or (2).

Approved.

(12) That Paragraph 13 be changed as follows:

1. Under (a), line 10, delete "or (d)" and insert "or" between (b) and (c).

2. Under (b), line 6, delete "or (d)" and insert the word "or" between (b) and (c).

Approved for first action of a change in an official method.

(13) That under Paragraph 16 (h), "Reagents", there be added the sentence, "A solution of sodium sulfide or of sodium thiosulfate of equivalent strength may be used".

Approved under suspension of the rules.

(14) That in Paragraph 18, "Determination", line 10, after "potassium sulfide" there be inserted "or sodium sulfide or sodium thiosulfate".

Approved under suspension of the rules.

(15) That in Paragraph 21, "Determination", line 8, after "potassium sulfide" add "or sodium sulfide or sodium thiosulfate".

Approved under suspension of the rules.

(16) That in Paragraph 23, "Determination", lines 3 and 4, "1 gram of mercuric oxide, or its equivalent in metallic mercury" be eliminated and "or approximately 0.7 gram of mercuric oxide (or its equivalent in metallic mercury)" substituted.

Approved under suspension of the rules.

(17) That in Paragraph 23, line 6, after the phrase "or until oxidation is complete" there be inserted "which usually requires not less than 2 hours".

Approved under suspension of the rules.

(18) That in Paragraph 23, line 7, after "potassium sulfide solution", there be inserted the words "sodium sulfide, or sodium thiosulfate" and after "solution" insert "if mercuric oxide or metallic mercury has been used".

Approved under suspension of the rules.

(19) That in Paragraph 26, "Determination", line 3, after "30 minutes" the phrase "with frequent shaking, or until complete solution results" be inserted.

Approved under suspension of the rules.

(20) That in Paragraph 28, "Determination", line 4, after "30 minutes with frequent shaking" the phrase "or until complete solution results" be inserted.

Approved under suspension of the rules.

(21) That in Paragraph 33, "Reduced Iron Method.—Official",



line 1, "1 gram" be eliminated and "0.7 gram or 1 gram" substituted therefor.

Approved under suspension of the rules.

(22) That in Paragraph 34, "Zinc-Iron Method.—Official", line 1, "10 grams" be eliminated and "7 grams or 10 grams" substituted therefor.

Approved under suspension of the rules.

(23) That in Paragraph 35, "Ferrous Sulfate-Zinc-Soda Method.—Official", line 1, "0.5 gram" be eliminated and "0.35 or 0.5 or 0.7 gram" be substituted therefor.

Approved under suspension of the rules.

(24) That the Devarda method for the determination of nitrogen in nitrate salt be adopted as a tentative method. The method is as follows:

Place 0.5 gram of the nitrate salt in a 600-700 cc. flask and add 300 cc. of water, 2 grams of the Devarda alloy, and 5 cc. of sodium hydroxide solution (42% by weight), pouring the sodium hydroxide down the side of the flask so that it does not mix at once with the contents.

Connect by means of a Davison scrubber—or other suitable scrubber bulb that will prevent the passing over of any portion of the spray—with a condenser, the tip of which always extends beneath the surface of the standard acid in the receiving flask. Mix the contents of the distilling flask by rotating and heat slowly at first and then at such a rate that the 250 cc. of distillate required will pass over in 1 hour. Collect the distillate in a measured quantity of standard acid and titrate with standard alkali solution, using cochineal or methyl red solution as indicator.

Approved.

(25) That in Paragraph 36, "Preliminary Test (Determination of Water-Insoluble Organic Nitrogen)", line 1, "1 gram" be eliminated and "1.4 grams or 1 gram" be substituted therefor.

Approved under suspension of the rules.

(26) That in Paragraph 37, "Determination", line 13, "this result" be eliminated and "the percentage of nitrogen" substituted therefor.

Approved under suspension of the rules.

(27) That in Paragraph 40 (b), "Platinum Solution", "For materials containing less than 15% of potash, a platinic chloride solution containing 0.2 gram of metallic platinum (0.42 gram of  $\text{H}_2\text{PtCl}_6$ ) in each 10 cc. is recommended", be added.

Approved under suspension of the rules.

(28) That in Paragraph 48, "Preparation of Solution", line 1, "5 (d)" be substituted for "5 (g)".

Approved for first action of change in an official method.

(29) That in Paragraph 50, "Volumetric Method.—Official", line 1, "5 (d)" be substituted for "5 (g)".

Approved for first action of change in an official method.

(30) That on page 14, the words "Citrate Acid-Soluble Phosphoric Acid" be substituted for "Citrate-Soluble Phosphoric Acid".

INORGANIC PLANT CONSTITUENTS.

SULFUR AND PHOSPHORUS IN THE SEEDS OF PLANTS.

It is recommended—

That the magnesium nitrate method for the determination of sulfur and phosphorus in plant materials<sup>1</sup> be made official. (First action as an official method.)

Approved.

ASH IN SEEDS.

It is recommended—

That the methods for the determination of iron and aluminium, calcium and magnesium<sup>2</sup> be further studied.

Approved.

*The following recommendations refer to revisions of the methods in the chapter on Inorganic Plant Constituents, Methods of Analysis, 1920.*

It is recommended—

(1) That the title of the chapter be changed from "Inorganic Plant Constituents" to "Plants".

Approved.

(2) That Paragraphs 2, 3, and 4 be deleted.

Approved.

(3) That Paragraph 4 be renumbered as Paragraph 2 and be changed to read as given in the report of the referee.

Approved.

(4) That Paragraphs 6, 7, and 8 be renumbered as 3, 4, and 5, respectively.

Approved.

(5) That Paragraphs 9, 10, 11, and 12 be deleted.

Approved.

(6) That the methods for sodium and potassium as given in Paragraphs 13, 14, and 18 be combined to read as given in the report of the referee and be renumbered as Paragraphs 6 and 7.

Approved.

(7) That the methods for chlorine under Paragraphs 15, 16, 17, and 20 be combined as given in the report of the referee and be renumbered as Paragraphs 8, 9, 10, and 11.

Approved.

(8) That the methods for sulfur and phosphorus, as recommended by the associate referee, be made official.

Approved.

(9) That the official method for sulfur in plants, the so-called sodium peroxide method, be deleted.

Not approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 415.

<sup>2</sup> *Ibid.*, 421.

REPORT OF SUB-COMMITTEE B ON RECOMMENDATIONS  
OF REFEREES, 1923.

By E. M. BAILEY (Agricultural Experiment Station, New Haven,  
Conn.), *Chairman*.

Chemical reagents, spices and other condiments (salad dressings, prepared mustard),  
drugs [acetylsalicylic acid; phenolphthalein; camphor and monobromated cam-  
phor; mercurials; turpentine oil; alkaloids; morphine, codeine, and diacetyl-  
morphine; procaine; medicinal plants; santonin; pollen grains; bitter  
tonics and laxative drugs; arsenicals; silver proteinates; cin-  
chona alkaloids; methylene blue; phenylcinchoninic acid  
(atophan); dimethylaminoantipyrine (pyramidon);  
barbital (veronal) and its derivatives].

CHEMICAL REAGENTS.

It is recommended—

That work on the chemical reagents be continued, and that the  
members of the association be urged to cooperate with the referee on  
this subject.

Approved.

SPICES AND OTHER CONDIMENTS.

SALAD DRESSINGS.

It is recommended—

That the methods for the examination of salad dressings, as described  
in the report of the referee this year, be adopted as tentative.

Approved.

PREPARED MUSTARD.

It is recommended—

(1) That the Hiltz-Hertwig method for the determination of crude  
fiber in prepared mustard, as outlined by the referee this year, with the  
exception that the reference to the crude fiber method there given be  
changed to designate the crude fiber method adopted as official this  
year, be adopted as an official method. (First action as an official  
method.)

Approved.

(2) That the present tentative method for crude fiber in prepared  
mustard be deleted.

Approved.

(3) That any change which may hereafter be made in the general  
official method for crude fiber shall automatically apply to and be made  
in the method for crude fiber in prepared mustard.

Approved.

## DRUGS.

(General recommendation of the sub-committee.)

The sub-committee recommends that no tests or assays for drugs be included in the A. O. A. C. methods of analysis unless such tests and assays differ substantially from those now recognized and defined in the United States Pharmacopeia or National Formulary, or unless such tests or assays are not included in these texts.

Approved.

## ACETYSALICYLIC ACID.

It is recommended—

(1) That the method for separating and determining acetylsalicylic acid in mixtures containing also caffeine and acetphenetidin, as described by the referee, be submitted for collaborative study during the coming year.

Approved.

(2) That the iodine method for total salicylates<sup>1</sup>, now tentative, be adopted as an official method. (First action as an official method.)

Approved.

(3) That the determination of acetylsalicylic acid in the presence of possible interfering substances, particularly laxatives, be studied.

Approved.

(4) That the associate referee, during the coming year, try to devise satisfactory methods for the determination of free and combined acetic acid.

Approved.

(5) That the tentative method for the quantitative determination of free salicylic acid<sup>1</sup> be considered by the referee with a view to its proper disposition.

Approved.

(6) That the bromine method for the determination of total salicylates<sup>1</sup> be studied by the incoming referee with a view to its proper disposition.

Approved.

(7) That the double titration method for the determination of acetylsalicylic acid<sup>2</sup> be studied by the incoming referee with a view to its proper disposition.

Approved.

## PHENOLPHTHALEIN.

It is recommended—

(1) That Methods I (iodination method) and II (ether-extraction

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 582.

<sup>2</sup> *Ibid.*, 583.

method), for the determination of phenolphthalein in tablets<sup>1</sup> be adopted as tentative.

Approved.

(2) That these methods be further studied as to their applicability to other varieties of phenolphthalein-containing drug products.

Approved.

#### CAMPBOR AND MONOBROMATED CAMPBOR.

It is recommended—

(1) That the methods suggested for the determination of camphor in pills and tablets<sup>2</sup> be studied during the coming year and suggestions made for further study or deletion, as may be advisable.

Approved.

(2) That the tentative methods adopted at the 1921 meeting<sup>3</sup> be made the subject of collaborative study during the coming year.

Approved.

#### MERCURIALS.

It is recommended—

That further study be made of the Rupp method<sup>4</sup> for the determination of mercuric chloride in tablets, with particular reference to the influence of citric acid.

Approved.

#### TURPENTINE OIL.

It is recommended—

(1) That the tentative fuming sulfuric acid method for mineral oil in turpentine oil<sup>5</sup>, as described by the referee, be adopted as an official method. (First action as an official method.)

Approved.

(2) That the tentative sulfuric acid-fuming nitric acid method for mineral oil in turpentine oil<sup>6</sup>, as described by the referee, be adopted as an official method. (First action as an official method.)

Approved.

(3) That the Grotlisch-Smith method<sup>7</sup> for coal tar oils in turpentine oil be further studied.

Approved.

#### ALKALOIDS.

It is recommended—

(1) That further collaborative study be made on methods for the separation of quinine and strychnine before adoption of the method as official.

Approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 7: 14.

<sup>2</sup> *Ibid.*, 1922, 5: 544.

<sup>3</sup> *Ibid.*, 587.

<sup>4</sup> *Chem. Ztg.*, 1908, 32: 1077.

<sup>5</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 466.

<sup>6</sup> *Ibid.*, 1922, 5: 552; 1923, 6: 466.

<sup>7</sup> *J. Ind. Eng. Chem.*, 1921, 13: 791.

(2) That the methods for the assay of physostigma and its preparations and the assay of fluid extract of hyoscyamus be not adopted as official methods in view of the recommendation pertaining to these methods as made by the committee in 1922<sup>1</sup>.

Approved.

(3) That methods<sup>2</sup> cited by the associate referee for the assay (a) of stramonium ointment, (b) of belladonna ointment, (c) of belladonna liniment, (d) of ipecac and its preparations, and (e) of atropine in tablets be further studied.

Approved.

#### MORPHINE, CODEINE, AND DIACETYLMORPHINE.

It is recommended—

(1) That the methods submitted (in 1922) for the qualitative and quantitative determinations of morphine, codeine, and diacetylmorphine<sup>3</sup> be adopted as official. (Final action.)

Approved.

#### PROCAINE.

It is recommended—

(1) That the two methods submitted (in 1922) for the determination of procaine<sup>4</sup> be adopted as official. (Final action.)

Approved.

#### MEDICINAL PLANTS.

It is recommended—

(1) That the recommendations, as made in the report of 1922<sup>5</sup>, be considered by the referee during the coming year and suggestions made for further study or discontinuance as may be desirable.

Approved.

#### SANTONIN.

It is recommended—

(1) That the tentative method for the detection of santonin in worm-seed<sup>6</sup> be studied by collaborators with a view to making it official.

Approved.

#### POLLEN GRAINS.

It is recommended—

That the method for the use of pollen grains as the means of identification of plants and plant products<sup>7</sup> be further studied.

Approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 268.

<sup>2</sup> *Ibid.*, 7: 1.

<sup>3</sup> *Ibid.*, 1921, 5: 150.

<sup>4</sup> *Ibid.*, 1922, 5: 590.

<sup>5</sup> *Ibid.*, 1923, 6: 269.

<sup>6</sup> *Ibid.*, 1922, 5: 557.

<sup>7</sup> *Ibid.*, 1921, 5: 157.

## BITTER TONICS AND LAXATIVE DRUGS.

It is recommended—

(1) That the study of methods for the assay of anthraquinone drugs and for the estimation of aloin and other plant principles be continued by the referee.

Approved.

## ARSENICALS.

It is recommended—

(1) That Method I for the determination of arsenic in arsphenamine and neoarsphenamine<sup>1</sup>, as described by the referee, be adopted as official. (Final action.)

Approved.

(2) That Method II for the determination of arsenic in arsphenamine and neoarsphenamine<sup>2</sup>, as described by the referee, be adopted as official. (First action as an official method.)

Approved.

(3) That a method be devised for the determination of arsenic in sodium cacodylate, since no assay is provided in the United States Pharmacopeia.

Approved.

## SILVER PROTEINATES.

It is recommended—

(1) That the quantitative and qualitative methods for silver in silver proteinates, as described by the referee, and other available methods be studied during the coming year.

Approved.

## CINCHONA ALKALOIDS.

It is recommended—

(1) That the method for the separation and estimation of the principal cinchona alkaloids, as described by the referee, be adopted as a tentative method.

Approved.

(2) That further collaborative work on this subject be discontinued.

Approved.

## METHYLENE BLUE.

It is recommended—

(1) That the method for the determination of moisture in methylene blue, as described by the associate referee, be studied collaboratively during the coming year.

Approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 462.

<sup>2</sup> *Ibid.*, 463.

(2) That the iodine volumetric method for the determination of medicinal methylene blue<sup>1</sup> be studied collaboratively

Approved.

PHENYLCINCHONINIC ACID (ATOPHAN).

It is recommended—

(1) That the method for the determination of atophan, as described by the referee, be adopted as a tentative method.

Approved.

(2) That the determination of atophan in mixtures be studied during the coming year.

Approved.

DIMETHYLAMINOANTIPYRINE (PYRAMIDON).

It is recommended—

(1) That qualitative tests, described by the referee as tests 1, 4, 5, and 6<sup>2</sup>, be adopted as tentative.

Approved.

(2) That the extraction method and the hydrochloride method for the determination of pyramidon<sup>3</sup> be studied collaboratively during the coming year.

Approved.

BARBITAL (VERONAL) AND ITS DERIVATIVES.

It is recommended—

That the method for the assay of barbitol and its derivatives, as described by the referee, be studied collaboratively during the coming year.

Approved.

SANDALWOOD OIL, ALCOHOL IN DRUGS, CHLOROFORM, AND  
CHLORAMINE PRODUCTS.

The committee repeats the recommendations of 1922 with regard to sandalwood oil, alcohol in drugs, chloroform, and chloramine products<sup>4</sup> with the suggestion that the referee consider these recommendations during the coming year and suggest further work or discontinuance, as may be advisable.

Approved.

A REVISION OF THE METHOD FOR THE DETERMINATION  
OF ATROPINE IN TABLETS.

It is recommended that the tentative method for the determination of atropine in tablets<sup>5</sup>, to be inserted in Chapter XXVIII, as par. 50 of the proposed revision of the *Book of Methods*, be changed to read, first line, "Weigh 25 to 100 tablets, etc".

Approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 7: 26.

<sup>2</sup> *Ibid.*, 30.

<sup>3</sup> *Ibid.*, 31.

<sup>4</sup> *Ibid.*, 6: 270, 271.

<sup>5</sup> *Ibid.*, 1920, 3: 379.



## REPORT OF SUB-COMMITTEE C, ON RECOMMENDATIONS OF REFEREES.

By W. C. GEAGLEY (Department of Agriculture, Lansing,  
Mich.), *Chairman*.

[Dairy products (moisture in cheese; methods for fat in malted, dried, and condensed milk), fats and oils, baking powder (fluorides in baking powder), eggs and egg products, coloring matters, metals in food (arsenic), pectin in fruits and fruit products, moisture in dried fruits, vinegars, flavors and non-alcoholic beverages, meat and meat products (separation of meat proteins, decomposition of meat products), gelatin, cereal foods, cacao products (microscopical examination of cacao products, chemical examination of cacao products, methods for the examination of cacao butter), and tea.]

### DAIRY PRODUCTS.

#### BABCOCK METHOD.

It is recommended—

(1) That the Babcock method submitted by the referee, which method includes I Apparatus, II Reagents, III Collection and Preparation of Samples, and IV Determination of Fat, be adopted as an official method, (first action as an official method), and that Sections 13, 14 and 15 of Chapter XXI, Dairy Products<sup>1</sup>, be deleted.

Further, that the portion of the method referring to the collection and preparation of samples of milk be placed at the beginning of the chapter under the heading "Milk", and that the portion referring to cream be placed under the heading "Cream", immediately preceding Section 22 of the *Book of Methods*<sup>2</sup>.

Approved.

(2) That the incoming Referee on Dairy Products confer with officials of the United States Bureau of Standards relative to the changes and amendments for Babcock glassware.

Approved.

(3) That the proposed changes and amendments in the Babcock method be subjected to collaborative study and investigation by the referee.

Approved.

(4) That this association cooperate in the study and perfection of methods for dairy products with the American Dairy Science Association, the American Public Health Association, and with other organizations that may be interested in this subject.

Approved.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 227.

<sup>2</sup> *Ibid.*, 230.

(5) That the incoming referee carry out the suggestions in the following motion offered by W. W. Randall, favorably acted upon by the association, and referred to this committee:

(1) That the Referee on Dairy Products be requested to discuss with the United States Bureau of Standards, the American Dairy Science Association, and the American Public Health Association the need for a standard 30%, 9-gram, short-neck, 6-inch cream-test bottle to supplement the several cream-test bottles already specified, and to report the result of such discussion at the next meeting of this association.

(2) That the referee be requested also to discuss with the Bureau of Standards and the two associations named the desirability of demanding a greater accuracy of graduation, in the case of the 50%, long-neck, 9-inch cream-test bottles, than has been specified, and to report the results of such discussion at the next meeting of this association.

(3) That the referee be requested also to discuss with the Bureau of Standards and the two associations named, the desirability of providing for a milk pipet, similar in every respect to the one specified in the report, except that it shall be graduated to deliver 17.45 ml. (or cc.) of water at 20°C., when drained in the manner prescribed by the Bureau of Standards for transfer pipets, and to report the result of such discussion at the next meeting of this association.

(4) That the referee be requested also to discuss with the two associations named the desirability of providing that the 18-gram charge of properly prepared milk may be weighed into the test bottle instead of being measured by means of the pipet.

Approved.

#### MOISTURE IN CHEESE.

It is recommended—

(1) That an associate referee be appointed to continue the study and collaborative work on the method for the determination of moisture in cheese<sup>1</sup>.

Approved.

#### METHODS FOR FAT IN MALTED MILK AND DRIED MILK.

It is recommended—

(1) That a further study be made of methods for dried milk, including the Jephcott modified Werner-Schmidt method<sup>2</sup>.

Approved.

#### FATS AND OILS.

It is recommended—

(1) That the modified Villavecchia test<sup>3</sup> be adopted as an official method. (Final action.)

Approved.

(2) That further work be done on the determination of acetyl value, including a study of the André-Cook method<sup>4</sup>.

Approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 498; 6: 136.

<sup>2</sup> *Analyst*, 1923, 48: 529.

<sup>3</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 265.

<sup>4</sup> *J. Am. Chem. Soc.*, 1922, 44: 392.

(3) That further work be done on the determination of unsaponifiable matter or residue including the method of Kerr and Sorber, as given in the report of the referee.

Approved.

(4) That the reworded Baudouin test for Sesame Oil<sup>1</sup> be adopted as an official method. (Final action.)

Approved.

(5) That the directions for the preparation of the Hanus iodine solution<sup>2</sup>, Section 15 (a), corrected by changing the sentence reading "Add 3 cc. of bromine to 200 cc. of acetic acid" to read "Add 3 cc. of bromine to 200 cc. of acetic acid and titrate 5 cc. of this solution against 0.1N sodium thiosulfate, adding 10 cc. of the potassium iodide solution (15 per cent) before titrating", be adopted as official. (Final action.)

Approved.

#### BAKING POWDER.

It is recommended—

(1) That the electrolytic method for the determination of lead, described by the referee in his report, be adopted as a tentative method, and that it be substituted for the electrolytic method given in Sections 33 and 34 of the present *Book of Methods*<sup>3</sup>.

Approved.

(2) That Method I "Colorimetric Method.—Tentative", Sections 28, 29, and 30; Method II.—Tentative, Section 31; and Method III.—Tentative, Section 32<sup>4</sup>, methods for the determination of lead in baking powders, be deleted from the methods of the association.

Approved.

(3) That the second paragraph under "Apparatus" of the volumetric method for the determination of carbon dioxide<sup>5</sup> be modified by changing the sentence, "a saturated solution of sodium chloride is prepared to which a small amount of sodium bicarbonate is added", to read "a nearly saturated solution of sodium chloride or sodium sulfate is prepared to which a small amount of sodium bicarbonate is added", and that under the heading "Total Carbon Dioxide<sup>6</sup>" the sentence "the decomposition flask is well rotated to secure intimate contact of materials, then allowed to remain at rest for 5 minutes", be changed to read, "the decomposition flask is well rotated and vigorously agitated to secure intimate contact of materials, then allowed to remain at rest for 5 minutes". With these changes, the method is recommended for adoption as a tentative method.

Approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 285.

<sup>2</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 244.

<sup>3</sup> *Ibid.*, 287, 288.

<sup>4</sup> *Ibid.*, 285, 286, 287.

<sup>5</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 453.

<sup>6</sup> *Ibid.*, 454.

(4) That the tentative Method II<sup>1</sup> for determining the neutralizing value of mono-calcium phosphate be changed to read as follows:

NEUTRALIZING VALUE OF MONO-CALCIUM PHOSPHATE.

*Method II.—Tentative.*

Weigh 0.84 gram of mono-calcium phosphate into a small beaker or casserole. Add 25 cc. of water and 5 drops of phenolphthalein (0.2% solution). Titrate with 0.2N sodium hydroxide to a faint pink, heat to boiling, boil 1 minute, and titrate while hot to a faint pink again. (Add bulk of alkali rapidly with vigorous stirring.) Total buret reading  $\times 2$  equals the neutralizing strength of 100 parts phosphate in terms of bicarbonate of soda.

Approved.

FLUORIDES IN BAKING POWDER.

It is recommended—

(1) That the tentative volatilization method for the determination of fluorine in baking powder<sup>2</sup>, adopted at the 1919 meeting, be reworded as given in the referee's report.

Approved.

(2) That the determination of a factor to place the recovery of fluorine on a 100 per cent basis be made the subject of further study.

Approved.

(3) That the referee study the two official gravimetric methods<sup>3</sup> for the determination of carbon dioxide in baking powders, with a view to determining whether both are used by analysts.

Approved.

EGGS AND EGG PRODUCTS.

It is recommended—

(1) That the methods—preparation of sample, moisture, ash, chlorides in ash as sodium chloride, organic and ammoniacal nitrogen, water-soluble protein-nitrogen precipitable by 40 per cent alcohol, fat, lipoids, and lipoid phosphoric acid, extraction and identification of added color, detection of the presence of whole egg or commercial yolk solids, and estimation of the percentage of egg solids, as compiled in the referee's report, be adopted as tentative methods.

Approved.

(2) That the chapter, entitled "Eggs and Egg Products", with a sub-head, "Egg Noodles", which will include the tentative methods adopted in Recommendation 1, be added to the next edition of the *Book of Methods*.

Approved.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 448.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1917, 9: 1116.

<sup>3</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 277.

(3) That the referee for the coming year study methods for the analysis of liquid, frozen, and dried eggs, and that he include the methods suggested in the referee's report.

Approved.

(4) That more data be collected for the basic value used in the formula to calculate egg solids in a noodle. This includes the analysis of a number of flour samples of the types used to manufacture noodles and samples of liquid, frozen, and dried whole eggs and commercial yolk.

Approved.

(5) That data on the values of the ratios used to distinguish a whole egg noodle from a commercial yolk noodle, be collected, summarized, and given with the method recommended to detect the presence of whole egg or commercial yolk solids in a noodle.

Approved.

(6) That the general referee on this subject be authorized to appoint such associates as he may deem advisable for the study of methods for the proposed chapter on "Eggs and Egg Products".

Approved.

#### COLORING MATTERS.

No report was submitted by the referee.

It is recommended—

(1) That investigational studies be undertaken to extend the tests given under Section 15 of Chapter X, *Book of Methods*<sup>1</sup>, to include the color dyes recently permitted under the regulations for the enforcement of the Food and Drugs Act.

Approved.

(2) That collaborative studies of the methods under Chapter X be begun, with the view to making them official.

Approved.

#### METALS IN FOODS.

It is recommended—

That the zinc-iron precipitation method for tin<sup>2</sup> be studied in comparison with the Baker-Sellars method<sup>3</sup>, and that extensive collaborative work be carried out with a view to making one or both of these methods official.

Approved.

#### ARSENIC.

It is recommended—

(1) That the Gutzeit method for arsenic, as modified to permit the use of hydrochloric acid as an alternative acid in the determination<sup>4</sup>, be adopted as an official method. (Final action.)

Approved.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 138.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 29.

<sup>3</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 150.

<sup>4</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 272.

(2) That a study be made of the action of arsine on organic and inorganic mercury compounds in order to obtain a more sensitive as well as a more stable agent for absorbing the evolved arsine.

Approved.

#### PECTIN IN FRUIT AND FRUIT PRODUCTS.

It is recommended—

(1) That the methods—preparation of sample solution, ash, alkalinity number, water-insoluble solids, alcohol precipitate, pectic acid, sulfur in ash, and total sulfur—recommended by the referee in his report, be adopted as tentative.

Approved.

(2) That the two methods for the determination of insoluble solids<sup>1</sup> and the method for the determination of alcohol precipitate<sup>2</sup> be deleted from the *Book of Methods*.

Approved.

(3) That the referee study the tentative methods for the determination of pectin in jellies, jams, and preserves submitted by the referee this year and also the method<sup>3</sup> for the determination of commercial glucose in fruit products.

Approved.

(4) That methods for the determination of fruit acids in fruit and fruit products be studied during the coming year, and that an associate referee be appointed for this study.

Approved.

#### MOISTURE IN DRIED FRUITS.

It is recommended—

That in view of pending studies on moisture determinations in other products the studies on this determination in dried fruits be discontinued and no referee be appointed.

Approved.

#### VINEGARS.

It is recommended—

(1) That the official method for alcohol<sup>4</sup> be amended by deleting the phrase, "add a small piece of paraffin", and adding the following sentence: "If the sample foams sufficiently to contaminate the distillate, a small piece of paraffin, preferably free of volatile constituents, may be added".

Inasmuch as this involves a change in an official method, which requires two actions, upon motion the by-laws were suspended and the action was made final.

Approved.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 154.

<sup>2</sup> *Ibid.*, 156.

<sup>3</sup> *Ibid.*, 155.

<sup>4</sup> *Ibid.*, 191.

(2) That the methods for total reducing substances before inversion, total reducing substances after inversion and non-volatile reducing substances (sugar), described by the referee in his report, be adopted as official methods, first action, and that Sections 8, 9, and 10 of Chapter XVIII, "Vinegars"<sup>1</sup>, be deleted from the present *Book of Methods*.

Approved.

(3) That the present tentative method for polarization, Section 12, Chapter XVIII, "Vinegars"<sup>1</sup>, be deleted and the method for polarization, using decolorizing carbons as described by the referee, be adopted as a tentative method. It is also recommended that this method be given further study.

Approved.

(4) That the official method for color, Section 20, Chapter XVIII, "Vinegars"<sup>2</sup>, be amended by adding the phrase, "or one-inch cell", so that the method will read, "Determine the depth of color in a Lovibond tintometer by good reflected daylight, using a one-half-inch or one-inch cell and the brewer's scale. Express the result in terms of a one-half-inch cell".

Inasmuch as this involves a change in an official method, which requires two actions, upon motion the by-laws were suspended and the action was made final.

Approved.

(5) That the method, "Color Removed by Fuller's Earth", as described by the referee, be adopted as an official method. (First action as an official method.)

Approved.

(6) That the method for the determination of sulfates, as described by the referee, be adopted as an official method. (First action as an official method.)

Approved.

(7) That the title of Section 18, reading "Fixed Acids.—Official"<sup>1</sup>, be changed to read "Non-volatile Acids.—Official", and that the sentence reading "One cc. of N/10 alkali is equivalent to 0.0067 gram of malic acid" be changed to read "One cc. of 0.1N alkali is equivalent to 0.0060 gram of acetic acid".

Inasmuch as this involves a change in an official method, which requires two actions, upon motion the by-laws were suspended and the action was made final.

Approved.

(8) That Section 19, "Volatile Acids.—Official"<sup>2</sup>, reading "To obtain the volatile acids subtract the fixed acids, calculated as acetic acid, from

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 193.

<sup>2</sup> *Ibid.*, 195.

<sup>3</sup> *Ibid.*, 194.

the total acid", be changed to read "To obtain the volatile acids subtract the non-volatile acids from the total acids".

Inasmuch as this involves a change in an official method, which requires two actions, upon motion the by-laws were suspended and the action was made final.

Approved.

(9) That the precautionary sentence, "The area of the dish exposed to the bath should not be greater in circumference than that covered by the liquid inside", be added to the method for the determination of glycerol<sup>1</sup>, following the sentence, "All evaporations should be made on a water bath, the temperature of which is maintained at 85°-90°C.".

Approved.

#### FLAVORS AND NON-ALCOHOLIC BEVERAGES.

No report was submitted by the referee.

It is recommended—

(1) That the referee give consideration to methods for the analysis of non-alcoholic flavors, as for example, the determination of orange oil and lemon oil in mineral oil, cottonseed oil, etc.

Approved.

(2) That the referee give consideration to the method adopted at the 1919 meeting of the association, as official, first action, for the determination of alcohol in orange and lemon extracts consisting only of alcohol, oil, and water<sup>2</sup>, to the end that final action may be taken on a method at the 1924 meeting.

Approved.

#### MEAT AND MEAT PRODUCTS.

It is recommended—

That the tentative method<sup>3</sup>, and the modification of the method<sup>4</sup>, for the determination of sugar in meat and meat products, as recommended by the referee at the 1921 and 1922 meetings, be studied during the coming year.

Approved.

#### SEPARATION OF MEAT PROTEINS.

No report was submitted by the referee.

It is recommended—

That cooperative work be done on the modified Van Slyke methods for the determination of amino acids in the globulin-albumin fractions of beef flesh, which were presented to the association at the 1921 meeting<sup>5</sup>.

Approved.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 192.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 308.

<sup>3</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 213.

<sup>4</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 72.

<sup>5</sup> *Ibid.*, 86.



DECOMPOSITION OF MEAT PRODUCTS.

No recommendations.

GELATIN.

It is recommended—

That the incoming referee continue the study of methods for the determination of copper and zinc.

Approved.

CEREAL FOODS.

It is recommended—

(1) That pending the conclusions of further study and collaborative work suggested by the referee in his report no change be made in the method for the determination of moisture in flour as printed in the present *Book of Methods*<sup>1</sup>.

Approved.

(2) That pending the conclusions of investigational and collaborative studies proposed by the referee no change be made in the official methods for the determination of ash as given in the *Book of Methods*<sup>1</sup>.

Approved.

(3) That an associate referee be appointed to make a study of methods of sampling flour for analysis and to devise a uniform and practical procedure for sampling.

Approved.

(4) That an associate referee be appointed to develop a method for determining the glutenin content of flour.

Approved.

CACAO PRODUCTS.

MICROSCOPICAL EXAMINATION OF CACAO PRODUCTS.

It is recommended—

(1) That the work of perfecting the microscopical method for the determination of cacao shells in cacao products<sup>2</sup> be continued.

Approved.

(2) That the use of Hertwig's solution as a mounting and clearing medium be included in the description of the method.

Approved.

CHEMICAL EXAMINATION OF CACAO PRODUCTS.

It is recommended—

That work be continued, preferably along the line of a "cold process" fiber determination.

Approved.

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 167.

<sup>2</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 257; 6: 99; 1923, 7: 141.

## METHOD FOR THE EXAMINATION OF CACAO BUTTER.

No report was submitted by the referee.

It is recommended—

That the recommendation made at the 1922 meeting for further study of the critical temperature of dissolution in acetic acid<sup>1</sup> and acetone-carbon tetrachloride<sup>1</sup> tests be continued.

Approved.

## TEA.

It is recommended—

(1) That the method for the determination of water extract in tea<sup>2</sup> be adopted as an official method. (Final action.)

Approved.

(2) That suggestions for further studies on tea be left to the incoming referee.

Approved.

## THIRD DAY.

## WEDNESDAY—AFTERNOON SESSION.

REPORT OF COMMITTEE TO COOPERATE WITH REVISION  
COMMITTEE OF THE UNITED STATES  
PHARMACOPEIA.

The suggestions made by the committee to the United States Pharmacopeial Committee for Revising the Tenth Revision, briefly summarized in the last annual report to this association, received careful consideration, and many of them are to be used.

The members of this committee have regularly received monographs containing the tentative texts to be used. Little of a critical nature has been received as a result of these monographs, owing, no doubt, to the satisfactory form in which they are prepared.

The question of using 20°C. as a basis for determining many of the constants required by the Pharmacopeia has been thoroughly considered, with the result that many of those interested desire that it be adopted. It is believed that 20°C. would be given preference if it were not for the fact that the rules governing the revision, adopted at the convention, direct that 25°C. shall obtain.

At the 1923 annual meeting of the American Society for Testing Materials the Sub-committee on Specific Gravity recommended that where there is no particular reason for using other values, 25°C. be adopted as the standard reference temperature. The association took no action on the recommendation during the meeting.

One of the obstacles to the adoption of either 20 or 25°C. as a reference temperature is that the Internal Revenue Law dealing with

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 279.

<sup>2</sup> *Ibid.*, 280.

liquors prescribes 60°F. as a basis. Plans are contemplated for having this changed, but, as may naturally be expected, there is some opposition.

In order that this association may have more concrete information regarding the present status of the next Pharmacopeia, attention is called to a number of features. More than three years have passed since the work of revision was begun, and all interested are naturally asking the question, "When will it be published?" This question can not be answered at present with any greater degree of definiteness than that it will probably appear within the next two years.

About 640 drugs are to be recognized in the next revision; 32 new drugs are to be added and 190 in the 9th Revision are to be deleted. In the 9th Revision, 243 were deleted. The chairmen of the sub-committees have submitted revised texts for all but about 100 of the admitted drugs, chemicals, and preparations.

It is proposed that the bio-assay methods shall be required, not optional. With two exceptions they are optional in the 9th Revision.

In order that these tests may be made more uniform in the hands of the various operators, the Bureau of Chemistry has offered to supply manufacturers with standard products for use as a comparison in applying the assays, and the Board of Trustees has authorized the placing of a statement in the preface of the Pharmacopeia, worded somewhat as follows:

In order to facilitate the adoption of the standards for biological assays prescribed by the Pharmacopeia, the Bureau of Chemistry of the United States Department of Agriculture has indicated its willingness to supply, upon application, for the purposes of comparative tests, substances conforming to said pharmacopeial standards.

The suggestion of placing "General Standards" as Part I of the Pharmacopeia is receiving favorable consideration. In the present revision this information appears under the heading "Introductory Notices". It is thought that this does not give these important features sufficient prominence. The suggestion made to prepare the text under headings so that the analyst can readily find the information desired, is also favorably received. Such headings and divisions as the following: "Description of Physical Properties", "Test for Identity", "Test for Impurities", "Assay", "Structure", "Powder", etc., may appear in the new text. The purity rubric will be used wherever practicable.

It is proposed to omit the molecular weights following chemical formulas in the purity statements. These are now duplicated in the molecular weight table in Part II.

It has been decided to use numerals only for quantities in formulas and omit the duplicated, spelled-out quantity. It is believed that this will make the printed formula more easily read.

Several proposed texts are submitted to illustrate these features:

## ACIDUM SULPHURICUM.

## SULPHURIC ACID.

## ACID. SULPHURIC.

Sulphuric Acid contains not less than 93 nor more than 95 per cent of  $\text{H}_2\text{SO}_4$ .

*Description and Physical Properties.*

A colorless, odorless liquid of oily consistence, very caustic and corrosive.

Specific gravity: about 1.83 at 25°C.

Sulphuric Acid is miscible with water or alcohol, with the evolution of much heat. The acid must be added with great caution to the diluent.

*Tests for Identity.*

When heated, the Acid is vaporized with the evolution of dense, white fumes.

Sulphuric Acid chars cane sugar, wood, and many other organic substances.

It is strongly acid to litmus paper, even when highly diluted.

*Tests for Impurities.*

Carefully superimpose a layer of ferrous sulphate T. S. upon 5 cc. of Sulphuric Acid, contained in a test tube, and cool the liquid. The zone of contact does not assume a brown or reddish-brown color (*nitric or nitrous acid*).

No precipitate is formed within an hour on mixing 1 volume of Sulphuric Acid with 4 or 5 volumes of alcohol (lead).

Sulphuric Acid conforms to the other tests for identity and purity given under *Acidum Sulphuricum Dilutum* when diluted to that strength.

*Assay*—Proceed as directed under the general assay for acids (Test —, page —), using about 1 cc. of the Acid, accurately weighed, and methyl orange T. S. as indicator.

Each cc. of normal sodium hydroxide used corresponds to 0.049045 Gm. of  $\text{H}_2\text{SO}_4$ .

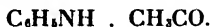
*Preserve* in glass-stoppered bottles.

*Preparations*—Acidum Sulphuricum Aromaticum, Acidum Sulphuricum Dilutum.

## ACETANILIDUM.

## ACETANILID.

Acetanil. Acetanilide. Antifebrin.

*Description and physical properties.*

Colorless, shining, crystalline leaflets, or a white, crystalline powder. It is odorless, has a slightly burning taste, and is stable in the air.

One Gm. of Acetanilid is soluble in 190 cc. of water, 3.4 cc. of alcohol, 3.7 cc. of chloroform, 17 cc. of ether, 4 cc. of acetone, 47 cc. of benzene, and in about 5 cc. of glycerin at 25°C.; in 20 cc. of boiling water and in 0.6 cc. of boiling alcohol. It is slightly soluble in petroleum benzin.

*Tests for identity.*

Acetanilid melts between 113° and 115°C.

Boil about 0.1 Gm. of Acetanilid with 5 cc. of sodium hydroxide T. S. The characteristic odor of aniline becomes noticeable. Add 1 cc. of chloroform, and heat the mixture. The disagreeable odor of phenyliso-cyanide (a poisonous substance) is evolved.

Boil about 0.1 Gm. of Acetanilid for several minutes with 2 cc. of hydrochloric acid. A clear solution results, which, when mixed with 3 cc. of an aqueous solution of phenol

(1 in 20), and 5 cc. of a filtered, saturated solution of chlorinated lime, acquires a brownish-red color. This becomes deep blue upon super-saturation with ammonia water.

Bromine T. S. produces a white, crystalline precipitate in an aqueous solution of Acetanilid.

*Tests for impurities.*

Ash; not more than 0.05 per cent.

Shake 1 Gm. of Acetanilid with 20 cc. of distilled water for two minutes and filter. The filtrate is neutral to litmus paper. On adding 5 drops of ferric chloride T. S. to 5 cc. of the filtrate, the color does not differ from that produced by adding 5 drops of ferric chloride T. S. to 5 cc. of distilled water (aniline salts).

The solution of 0.5 Gm. of Acetanilid in 5 cc. of sulphuric acid is colorless or only faintly yellow (readily carbonizable substances).

*Average dose*—Metric, 0.2 Gm.—Apothecaries, 3 grains.

**BELLADONNÆ RADIX.**

**BELLADONNA ROOT.**

**BELLAD. RAD.**

Belladonna Root is the dried root of *Atropa Beladonna* Linné (Fam. *Solanaceæ*).

It yields not less than 0.45 per cent of the total alkaloids of Belladonna Root and contains not more than 10 per cent of its stem bases, woody crowns, or other foreign organic matter. It yields not more than 1 per cent of acid-insoluble ash.

Cylindrical or tapering, sparingly branched, often split longitudinally or broken transversely; 0.5 to 4 cm. thick; light grayish brown color externally, nearly white internally; somewhat wrinkled longitudinally and the soft periderm frequently abraded; fracture short, mealy, and emitting a puff of dust consisting chiefly of starch grains; nearly odorless when dry, somewhat narcotic when moistened; taste sweetish, then bitterish and acrid.

*Structure*—Cork, a few layers of thin-walled cells; large crystal cells, filled with micro-crystalline calcium oxalate, and relatively numerous in the younger roots, scattered through the abundant, starch-bearing parenchyma of the bark and wood; large, porous or reticulate tracheæ in scattered groups and, in the older roots, associated with wood fibers; cambium layer conspicuous; the medullary rays 1 to 5 cells wide.

*Powder*—Ash-gray to light brown; starch grains numerous, simple, and compound, the single grains up to 0.030 mm. in diameter and with a distinct, somewhat excentric hilum, the polarizing bands increasing in distinctness in direct ratio of the size of the grains; numerous sphenoidal micro-crystals 0.003 to 0.010 mm. long; fragments of tracheæ and wood-fibers few; long, thin-walled, slightly lignified bast-fibers from Belladonna stem very few. Old fibrous roots produce an excess of lignified tissue.

*Assay*—Take 15 Gm. of Belladonna Root in No. 60 powder and proceed by Type-Process B. Use ether-chloroform mixture in the first percolation of the drug and chloroform for extracting the alkaloids from the aqueous liquid.

Determine the alkaloids volumetrically. Each cc. of tenth normal sulphuric acid consumed corresponds to 28.9 milligrams of the total alkaloids of Belladonna Root. (See Proximate Assays, p. —).

Abstracts of some of the proposed organic and inorganic chemical texts have been published<sup>1</sup>. Reprints of these may be obtained from the chairman, E. Fullerton Cook, 636 South Franklin Square, Philadelphia, Pa. Abstracts of proposed changes of additional texts may also

<sup>1</sup> *J. Am. Pharm. Assoc.*, 1923, 12: 57, 991.

be obtained from Chairman Cook. They are available for publication in *The Journal* of this association if desired. These abstracts cover most of the titles in the following classes: Botany, Inorganic and Organic Chemicals, Volatile Oils, Extracts and Fluidextracts, Waters, Solutions, Spirits, Sirups, Cerates, Ointments, Miscellaneous Galenicals, and Nomenclature.

It may be interesting to note that the physicians and pharmacists of Cuba are taking part in this revision and that the 9th Revision has been translated into Spanish and Chinese.

L. F. KEBLER,                      H. C. FULLER,  
H. C. LYTHGOE,                  A. R. BLISS.

*Committee to Cooperate in Revision of  
the U. S. Pharmacopeia.*

## REPORT OF THE REPRESENTATIVES ON THE BOARD OF GOVERNORS OF THE CROP PROTECTION INSTITUTE OF THE NATIONAL RESEARCH COUNCIL<sup>1</sup>.

As treatment of cereal seeds for smut control, the Institute arranged for extensive cooperative testing of copper carbonate in comparison with copper sulfate and lime, and formaldehyde. In 1922 the difficulty with the formaldehyde was that it tended to reduce yields of wheat and oats, whereas the copper compound dusts did not: they controlled smut fairly well. Nickel carbonate also was found to have some fungicidal value. The work was continued in 1923.

After two seasons, the cooperative experiments in dusting apple trees were discontinued during 1923.

Valuable results have already come from the sulfur investigations. A discovery of an active fungicidal agent was of such importance that to protect the public patent claims were filed for the Institute in the United States, Canada, England, and France. Recent work has disclosed, also, a new form of contact insecticide that promises to be of much service in controlling certain insects.

A season's testing of a calcium arsenate for fungicidal purposes was provided for by Riches, Piver and Company.

Quaker Oats Company, through the Miner Laboratories, Chicago, are financing a year's research of the value of an organic mercury compound for pest control purposes.

"Phinotas Disinfectant", manufactured by the Phinotas Chemical Company of New York, is a miscible oil that is being investigated as an insecticide.

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<sup>1</sup> Presented by P. S. Burgess.

The B. G. Pratt Company of New York is meeting the expenses of an extensive study of "Scalecide" during a period of three years.

Many industrial concerns feel that the Institute, because of its knowledge of appropriate laboratory equipments and skilled supervisors, is in a position to render to them and to the public an unbiased service which can not be equalled in any other way.

BURT L. HARTWELL,  
H. J. PATTERSON.

Approved.

### REPORT OF THE SECRETARY-TREASURER.

By W. W. SKINNER (Bureau of Chemistry,  
Washington, D. C.).

As it has been the duty of the secretary-treasurer in the past to stress the troubles that have retarded the progress of the association, so this year it is his privilege and pleasure to report an improvement in its financial condition and a distinct evidence of unusual and important progress in its work.

The bank balance in 1922 was \$216.87; this year it is \$414.54. As a result of a campaign to enlist those institutions that had not paid dues heretofore but which are eligible to membership the number has been increased from 53 to 61. Expenditures have been kept at a minimum, and no unusual bills have had to be paid.

All the proceedings for this year have been published, and *The Journal* has issued on scheduled time. The affairs of *The Journal* have been presented in detail by R. W. Balcom, Chairman of the Board of Editors, but it is well to emphasize that the proceedings do not fill the four numbers of the volume and that space is available, therefore, for contributed papers. A regular and dependable supply of outside matter would help materially in making an interesting journal and increasing the number of subscriptions.

The changes of refereeships during the year were the following: A. L. Prince was appointed as Referee on Nitrogen to take the place of I. K. Phelps, resigned; H. M. Lancaster was appointed as Referee on Maple Products; L. C. Mitchell, Referee on Moisture in Cheese, and M. G. Wolf, Referee on Food Preservatives, resigned, but the vacancies were not filled; F. C. Blanck was appointed Referee on Canned Foods but did not accept, and no other appointment was made; C. B. Lipman resigned, and W. H. MacIntire was appointed Chairman of the Committee on Revision of Methods of Soil Analysis; and E. V. Lynn was

appointed as Referee on Methods for the Determination of Alcohol in Drugs.

Considerable correspondence relating to the accuracy of the procedure for carrying out the Babcock test for fat in milk and cream was carried on with E. M. Bailey, C. L. Alsberg, State Officials of California, O. F. Hunsiker, and others. The opinion is quite general that this test gives results too high, and there also seem to be discrepancies owing to the difference in the standardization of the glassware and method of reading. The matter was finally referred to J. Hortvet, the Referee on Dairy Products, and a committee was appointed consisting of J. Hortvet, E. M. Bailey, and W. W. Randall to represent the Association of Official Agricultural Chemists and of A. O. Dahlberg, O. F. Hunsiker, and F. W. Bouska to represent the American Dairy Science Association.

As a result of the work of this committee the procedure has been carefully revised, as presented to the association by the Referee on Dairy Products.

Severe criticism of the association's methods for testing the moisture content of flours has arisen. Attention has been drawn to the fact that the present methods are unsatisfactory. This matter was brought to the attention of the Referee on Cereal Foods.

The Executive Committee has held two meetings and transacted other necessary business by correspondence. A committee, composed of the Editor of *The Journal* and the Secretary-Treasurer of the Association, was appointed to devise a plan for financing the second revised edition of the *Book of Methods*. This committee considered a proposal to issue a students' edition at a reduced price but concluded, as did a former committee, that to do so would be unwise from a financial standpoint. The committee, however, was authorized to grant the usual book dealers' discount of 20 per cent to teachers for orders of ten or more volumes for classroom work, upon receipt of satisfactory evidence that the books are to be used for this purpose.

The committee provided for the appointment of a new committee to study methods of sampling and also of a referee to study methods for analyzing naval stores. The advisability of the association considering methods of analysis for paints and oils was discussed.

The financial statement will be found on page 210.



## REPORT OF COMMITTEE TO COOPERATE WITH OTHER COMMITTEES ON FOOD DEFINITIONS.

This committee respectfully submits the following report of the proceedings of the Joint Committee on Food Definitions and Standards for the period following the 1922 meeting of this association.

There have been no changes either in personnel or policy of the committee during the past year. Two meetings have been held since the last report, which was presented in November 1922. Final affirmative action has not been taken on any schedules affecting foods or drugs with the exception of the following revised and amended definitions and standards for ground mustard seed, mustard cake, mustard flour, and prepared mustard, adopted at the meeting held March 12-16, 1923. The revised definitions and standards were published from the Office of the Secretary of Agriculture under date of June 9, 1923, in the following form:

**GROUND MUSTARD SEED, MUSTARD MEAL.**

*Ground Mustard Seed, Mustard Meal*, is the unbolted, ground mustard seed and conforms to the standards for mustard seed.

**MUSTARD CAKE.**

*Mustard Cake* is ground mustard seed, mustard meal, from which a portion of the fixed oil has been removed.

**MUSTARD FLOUR, GROUND MUSTARD, "MUSTARD".**

*Mustard Flour, Ground Mustard, "Mustard"*, is the powder made from mustard seed with the hulls largely removed and with or without the removal of a portion of the fixed oil. It contains not more than one and five-tenths per cent (1.5%) of starch, nor more than six per cent (6%) of total ash.

*Prepared Mustard* is a paste composed of a mixture of ground mustard seed and/or mustard flour and/or mustard cake, with salt, vinegar, and with or without sugar (sucrose), spices, or other condiments. In the fat-, salt-, and sugar-free solids it contains not more than twenty-four per cent (24%) of carbohydrates, not more than twelve per cent (12%) of crude fiber, nor less than five and six-tenths per cent (5.6%) of nitrogen, the carbohydrates being calculated as starch.

At the meeting held in March the subject of ice cream was considered, and much time was devoted to a discussion of a tentative schedule of definitions and standards. This subject presented unusual difficulties, owing partly to the multiplicity of views existing in the various States regarding composition and standards for various types of ice cream. Repeated inquiries have been received from State and city food-enforcement officials who are anxious to learn whether the Federal authorities reaffirm or contemplate a revision of the present schedule covering this class of products. The situation existing throughout the entire country has emphasized in the minds of the committee the urgent necessity of arriving at some definite conclusion at an early date. The entire sub-

ject of ice cream has been given a careful study, and considerable progress has been made, but a final decision has not yet been reached on any portion of the schedule on account of the necessity of postponing action until a later meeting of the committee. At the same meeting the subject of flour was brought forward for discussion, and a plan was considered for a thorough investigation with a view to the preparation of a tentative schedule to serve as a basis for a conference with the millers and the trade. Also a conference was held jointly with representatives of the Bureau of Animal Industry on the subject of a proposed schedule of definitions and standards for meat products following which the committee devoted some time to a discussion of the schedule, with the result that many important alterations were introduced into a number of definitions.

At the meeting held in August, 1923, the jams and jellies schedule was considered, and an important brief on the subject was submitted to the committee by a representative of the National Preserving and Fruit Products Association. The greater portion of the time of the meeting was devoted to a discussion of the meat schedule with reference partly to definitions now in force in the Bureau of Animal Industry. A revised draft of the schedule was submitted to the bureau on July 27, 1923, and returned to the committee on August 7, 1923, with the comments of the bureau. It is hoped that a satisfactory schedule covering these products will be affirmed at an early date.

During the same meeting action was taken by the committee with respect to a change that for sometime past has been deemed necessary in the standard for cider vinegar. It has been the experience of the Bureau of Chemistry and a number of the State food laboratories that occasionally genuine cider vinegars fail to meet the requirements of the numerical standards with regard to the total solids, soluble phosphoric acid, and to a limited extent the alkalinity of the ash and the rotation. For this reason, the committee unanimously decided to amend the standard eliminating the numerical limitations, with the exception of the requirement of 4 grams of acetic acid per 100 cc. The vinegar standard, as amended and adopted, now reads:

*Vinegar, Cider Vinegar, Apple Vinegar*, is the product made by the alcoholic and subsequent acetous fermentation of the juice of apples; and contains, in one hundred cubic centimeters (100 cc.), at 20°C., not less than four (4) grams of acetic acid.

Other problems were discussed in a preliminary way in connection with the schedules for jams and jellies and for flours and meals, and plans were considered for a further study of these subjects.

JULIUS HORTVET,      C. D. HOWARD.  
E. M. BAILEY,

*Committee to Cooperate with Other  
Committees on Food Definitions.*

Approved.

## REPORT OF AUDITING COMMITTEE.

The Auditing Committee has examined the financial report of the Secretary-Treasurer, submitted by W. W. Skinner, covering the period from November 1, 1922 to November 1, 1923, and found it correct, with proper and sufficient vouchers for all disbursements.

The committee has also examined the financial report on publications, submitted by R. W. Balcom, Chairman of the Board of Editors, covering the period from November 1, 1922 to November 1, 1923, and found it correct, with proper and sufficient vouchers for all disbursements.

G. L. BIDWELL,                      C. S. CATHCART.  
J. J. T. GRAHAM,

*Auditing Committee.*

Approved.

## REPORT OF NOMINATING COMMITTEE.

The Committee respectfully submits the following names:

*President:* R. E. Doolittle, Chicago, Ill.

*Vice President:* C. A. Browne, Washington, D. C.

*Secretary-Treasurer:* W. W. Skinner, Washington, D. C.

*Additional Members of the Executive Committee:* E. M. Bailey, New Haven, Conn., and P. B. Dunbar, Washington, D. C.

C. H. JONES,                      B. B. ROSS.  
F. P. VEITCH.

*Nominating Committee.*

It was moved, seconded, and carried that the secretary be directed to cast a unanimous ballot for the officers nominated.

## REPORT OF COMMITTEE ON RESOLUTIONS.

Since the last meeting, the association has lost by death two of its former members.

Dr. Fritz Wilhelm Woll, Professor of Animal Nutrition, University of California, well known as a writer on animal feeding and dairy subjects, died at Berkeley, Calif., December 6, 1922.

Dr. Woll was for many years connected with the work of the Agricultural Experiment Station of the University of Wisconsin and of the College of Agriculture of the same institution, while for some years past he had occupied the chair at the University of California that he was so successfully filling at the time of his death.

For a number of years Dr. Woll participated actively in the work of this association, discharging with efficiency and fidelity the duties devolving upon him in various important posts, including that of president, and contributing much to the successful outcome of the efforts of the organization in securing improved methods for the analysis of materials and products of importance to agriculture.

As an author, Dr. Woll made notable contributions to the literature of various phases of agricultural chemistry, while his numerous bulletins and papers on subjects connected with his special field of work gave him an enviable position among his fellow workers in the same field of scientific endeavor.

As it is fitting that our organization should place on record an expression of the sense of loss which the association has sustained,

*Therefore, be it resolved,* That in the death of Dr. Woll, this association has lost a former officer and member, whose efforts were an important factor in the early progress of this association; the cause of agricultural science has lost a leader and worker who, in the laboratory and lecture room as well as with his pen, aided largely in promoting a wider dissemination of a knowledge of the principles of scientific agriculture throughout the country, while those who had the privilege of knowing him intimately have lost a friend, loyal and true, whose memory will be warmly cherished.

*Resolved, further,* That these resolutions be published in the proceedings of the association and that a copy be transmitted to the family of our deceased co-worker.

Dr. Frank C. Cook, chemist of the Bureau of Chemistry for twenty years, died at Dallas, Texas, on June 19, 1923, following an operation for appendicitis.

As a member of the association for about twenty years, Cook was a frequent participant in its work, and repeatedly served as an able and efficient referee.

Your committee recommends the adoption of the following resolution:

*Resolved,* That in the death of Dr. Frank C. Cook this association has lost a valuable active member—one who rendered unselfish and efficient service in the development of methods of analysis now used by this association.

*Resolved,* That in the passing of Dr. Cook many of us have lost a warm personal friend.

*Resolved,* That these resolutions be published in the proceedings of this association and that a copy be sent to the family of our deceased brother member and friend.

*Resolved*, That this association expresses to the Honorable Henry C. Wallace its appreciation of his inspiring and encouraging address, and its thanks for his kind words of approval of its work.

*Resolved*, That this association expresses to its honorary president, H. W. Wiley, its pleasure at his continuing interest in its welfare and its work and its appreciation of his presence and of his delightful and inspiring address.

*Resolved*, That this association desires to record its appreciation of the impartial, business-like, and courteous manner in which the president, A. J. Patten, has discharged the duties of his office.

*Resolved*, That this association is indebted to the Chairman of the Board of Editors, R. W. Balcom, for the excellent preparations made for this convention and for the efficient manner in which the affairs of *The Journal* have been conducted.

*Resolved*, That the association wishes to commend the efficient work of the secretary, W. W. Skinner, and his various assistants for their untiring and highly successful efforts in making this convention worth while.

*Resolved*, That this association desires to record its appreciation of the untiring and unselfish work of the Chairman of the Committee on Editing Methods of Analysis, as well as the efforts of his co-workers, especially in the work of revision of the *Book of Methods*.

*Resolved*, That the thanks of this association are due the management of the Raleigh Hotel for the use of the various rooms and other courtesies extended to its members.

*Resolved*, That this association wishes again to go on record as heartily endorsing the campaign inaugurated by the American Chemical Society to educate the American people to a better understanding of chemistry, its possibilities, and its applications to every-day life.

R. N. BRACKETT,      P. S. BURGESS.  
J. W. KELLOGG,

*Committee on Resolutions.*

Approved.

## CONTRIBUTED PAPERS.

### ESTIMATION OF STARCH AND SUGARS BY THE USE OF PICRIC ACID.

By MAYNE R. COE, *Associate Chemist*, and G. L. BIDWELL, *Chemist in Charge* (Cattle Food Laboratory, Bureau of Chemistry, Washington, D. C.).

The present methods for determining starch and sugar in feeding stuffs and similar materials are unsatisfactory; they are laborious, time-consuming, and none too accurate. In an attempt to eliminate these undesirable features the picric acid colorimetric method, which has heretofore been used in biological analyses, was studied.

Up to this time, no attempt has been made to apply the color reaction specifically to the determination of starch. Braun<sup>1</sup> and Johnson<sup>2</sup> first observed the reaction; Lewis and Benedict<sup>3</sup> successfully applied it for the estimation of sugar in the blood; Dehn and Hartman<sup>4</sup> used it for the determination of various sugars; Rose<sup>5</sup> applied it to the inversion and determination of cane sugar; Myers and Croll<sup>6</sup> made use of it for the determination of carbohydrates in vegetable foods; Bernhard<sup>7</sup> adapted it to the determination of free reducing sugar and total carbohydrates in miscellaneous food materials; and Benedict and Osterberg<sup>8</sup> used it, with modifications, for the determination of sugar in normal urine.

The determination of starch or sugar by this method depends upon the formation of a yellowish red or yellowish brown color. When solutions of sugars are heated with picric acid and an alkali, the depth of color is proportional to the amount of sugar present and may be compared to a selected standard. Sodium hydroxide was used as the alkali, but it proved unsatisfactory owing to the caramelization of the sugar. This trouble was avoided by Dehn and Hartman through the use of sodium carbonate. It was found that in order to obtain good results, it is necessary that the solutions when finally prepared for reading be a few shades darker than the standard and contain between 0.4 and 1.2 milligrams of dextrose. This feature enables the analyst to make determinations on small samples or on those containing small amounts of sugar or starch.

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<sup>1</sup> *Z. Chem.*, 1865, 1: 744.

<sup>2</sup> *British Med. J.*, 1883, 1: 504.

<sup>3</sup> *J. Biol. Chem.*, 1915, 20: 61.

<sup>4</sup> *J. Am. Chem. Soc.*, 1914, 36: 403.

<sup>5</sup> *J. Biol. Chem.*, 1921, 46: 529.

<sup>6</sup> *Ibid.*, 637.

<sup>7</sup> *Sugar*, 1915, 17: 41.

<sup>8</sup> *J. Biol. Chem.*, 1921, 48: 51.

Mucilaginous substances, such as are found in linseed cake, apple pomace, pectin pulp, etc. (polysaccharides), polyphenols, aldehydes, ketones, and purine bases, as well as the coloring materials in molasses and the like, give high results. Special treatment, however, often eliminates these substances and allows true values for starch to be obtained.

In the first application of this method for starch, taka-diastrase was used, but after repeated trials it was found that uniform results could not be obtained even with the freshly prepared enzyme. Edward Horton<sup>1</sup> states: "The taka-diastrase method<sup>2</sup> of estimating starch can not be implicitly trusted,—it is necessary to make test experiments on pure starch with every sample of enzyme, both before use and during the time it is kept". When the work was repeated with malt diastase, uniform results were obtained.

When this method is applied to sugars that require hydrolysis, use is made of the hydrolyzing properties of picric acid. In the case of reducing sugars, the development of the color is obtained immediately when alkali is added to the solution. With non-reducing sugars the alkali is not added until after the hydrolysis by picric acid. The results then show total sugars as reducing sugars. The value obtained by subtracting the figure for reducing sugars from that for total sugars, multiplied by the factor in Table 3, will give the amount of that particular sugar known to be present. This feature of the method is one that saves considerable time in comparison with the method of hydrolysis by hydrochloric acid.

The authors believe that those engaged in analyzing foods and feeding stuffs will find the methods described in this paper of use for the following reasons:

- (1) Starch or sugar may be determined in small samples or in materials containing small amounts of either.
- (2) The time consumed in a determination is notably less than in the copper reduction method.
- (3) Preparation of crucibles is avoided, no bulky solutions are required, and the manipulation is simplified.

The method follows:

#### METHOD FOR STARCH.

##### REAGENTS.

- (a) *Dry picric acid of good grade.*
- (b) *Saturated sodium hydroxide solution.*
- (c) *22% sodium carbonate solution.*
- (d) *0.02% pure dextrose solution saturated with picric acid as the standard. (This solution will keep indefinitely in the dark.)*

<sup>1</sup> *J. Agr. Sci.*, 1921, 11: 240.

<sup>2</sup> *Davis and Daish. J. Agr. Sci.*, 1914, 6: 152.

(e) *Malt solution*.—Grind 5 grams of malt for every 80 cc. of solution needed. Add the necessary water and digest for 2 hours with frequent shaking. Filter. (If an electric high-speed stirrer is available the time is shortened to 20 minutes.)

#### PROCEDURE.

Grind the material to pass a 40-mesh sieve and thoroughly mix. Weigh out an amount of the sample that will contain from 0.25 to 0.45 of a gram of starch. Transfer the sample to a filter paper—such as No. 589 Blue Ribbon S.—fastened to a funnel by a paper clip, and extract 5 or 6 times with ethyl ether. Repeat the extraction with 150 cc. of 35% alcohol to rid the sample of soluble proteins, fats, sugars, etc. (Often it is well to extract again with ether and allow to dry since alcohol inhibits the action of the diastase in the malt digestion.)

Place the filter paper and sample in a 300 cc. volumetric flask, add about 20 cc. of cold distilled water to wet the sample thoroughly, and then add about 100–120 cc. of actively boiling distilled water<sup>1</sup>. (Wetting the sample first with cold water and then with actively boiling water bursts the starch grains and permits a more complete gelatinization and inversion of the starch; it also keeps the sample from frothing.) From this point run a blank with each determination and treat in every respect like the sample, beginning with water and a filter paper.

Gelatinize 30–60 minutes. Cool below 55°C. and add, by means of a pipet, 20 cc. of newly prepared malt solution. Place the flasks in a water bath, the temperature of which can be regulated; heat gradually to 70°C. (one-half hour will be necessary); and maintain at this temperature for one-half hour; raise to and keep at 80°C. for ten minutes and finally sterilize at boiling temperature for 5 minutes. Cool below 55°C., add another 20 cc. portion of fresh malt solution, keeping the bath at 55°C. for 1 hour, and then raise the temperature to 100°C. Remove the flask, allow to cool, and make up to mark. Mix thoroughly and filter.

Transfer the necessary aliquot of the filtrate (5, 10, 15, or 20 cc. according to the percentage of starch estimated) to a Nessler tube graduated to 25 cc. and add 1.4 cc. of concentrated hydrochloric acid, making the acidity about 0.6N when of 20 cc. volume. If less than 20 cc. of the filtrate is used, always make up to that volume with distilled water in order to have the proper concentration of acid. After covering the tube with an inverted funnel to prevent evaporation and condensation, hydrolyze in the steam bath from 1–2 hours and cool to room temperature.

When the approximate starch content of a sample is uncertain it is suggested that extra portions (5 or 10 cc.) of the filtrate used for hydrolyzing be set aside for future use in case the first portion should prove to be outside the limits of the method. Make up the extra solutions for hydrolysis to about 20 cc. and add 1.4 cc. of concentrated hydrochloric acid to prevent spoilage.

Nearly neutralize with a saturated sodium hydroxide solution, using litmus paper as indicator and being careful not to allow an appreciable rise in temperature. Do not use a weaker solution of sodium hydroxide because, if weaker, the amount of solution needed to neutralize the acid after hydrolysis may bring the solution above the 25 cc. mark. If an excess of alkali is used add hydrochloric acid until the solution becomes slightly acid. Make up to 25 cc., shake well, and add enough dry picric acid, usually about 0.3 gram, to make a saturated solution. Allow to stand, with frequent shaking, for about 15 minutes; filter.

Pipet 3 cc. of the standard solution and 3 cc. of the sample, to each of which has been added from 1–2 cc. of 22% sodium carbonate solution, in Nessler tubes graduated to 5, 15, 20, 30, and 50 cc., and heat for 10 minutes in a steam or water bath. (A color

<sup>1</sup> Walton and Coe. *J. Agr. Research*, 1932, 23: 995.



develops that is proportional to the amount of dextrose present. Note that when the temperature of the water bath is lower than 98°C. the color of the solutions is not developed to the fullest intensity, and the results are therefore adversely affected.) Compare the colors in a suitable colorimeter—the Bock-Benedict may be recommended for ordinary purposes.

The percentage of starch in materials free from interfering polysaccharides is calculated by the following formulas:

X = Per cent of starch,

P = Uncorrected figure for starch calculated as dextrose,

A = Original volume (300 cc.),

B = Volume taken for hydrolysis,

C = Volume to which B is diluted (25 cc.),

D = Volume of C taken (3 cc.),

E = Volume to which D is diluted,

F = Final volume of standard (30 cc.),

R<sub>1</sub> = Reading of standard,

R<sub>2</sub> = Reading of sample, and

W = Weight of sample originally taken.

Then—

$$P = \frac{A \times C \times E \times R_1 \times 0.0006 \times 100}{B \times D \times F \times R_2}.$$

Simplifying—

$$P = \frac{300 \times 25 \times E \times R_1 \times 0.06}{B \times 3 \times 30 \times R_2}, \text{ and}$$

$$P = \frac{5 \times E \times R_1}{B \times R_2}. \quad (1)$$

To correct for the reducing material in the reagents the following calculation is made on the blank:

P' = Dextrose in the blank,

A' = Original volume of blank (300 cc.),

B' = Volume of blank taken for hydrolysis,

C' = Volume to which B' is diluted (25 cc.),

D' = Volume of C' taken (3 cc.),

E' = Volume to which D' is diluted,

F' = Final volume of standard (30 cc.),

R<sub>1</sub> = Reading of standard, and

R<sub>2</sub> = Reading of blank.

Then—

$$P' = \frac{A' \times C' \times E' \times R_1 \times 0.0006 \times 100}{B' \times D' \times F' \times R_2}.$$

Simplifying—

$$P' = \frac{5 \times E' \times R_1}{B \times R_2}. \quad (2)$$

Then—

$$X = \frac{0.9 (P - P')}{W}. \quad (3)$$

*Starch in the Presence of Interfering Polysaccharides.*

Transfer 20 cc. of filtered solution after the malt digestion to a 100 cc. volumetric flask and make up to volume with 95% ethyl alcohol. Mix well and filter off the precipitated material. Evaporate 90 cc. of this filtrate on the steam bath to about 10 cc. or until only a trace of alcohol is left. (An electric fan shortens the time.) Take up with water and transfer to a Nessler tube graduated to 25 cc., make up to 20 cc., add 1.4 cc. of concentrated hydrochloric acid, and hydrolyze in the steam bath for 1-2 hours. From this point proceed as in the above method. Treat the blank in all respects the same as the sample to which it applies.

For starch in the presence of interfering polysaccharides calculate as follows:

M = Volume taken to dilute to 100 cc. with alcohol (20 cc.),

N = Final volume of M (100 cc.),

L = Volume of filtrate taken for evaporation (90 cc.), and

J = Volume to which L is diluted after evaporation (25 cc.).

Then—

$$P = \frac{A \times N \times J \times E \times R_1 \times 0.0006 \times 100}{M \times L \times D \times F \times R_2}$$

Simplifying—

$$P = \frac{25 \times E \times R_1}{3 \times F \times R_2} \quad (4)$$

The simplified formula for the blank is as follows:

$$P' = \frac{25 \times E' \times R_1}{3 \times B' \times R_2} \quad (5)$$

Then—

$$X = \frac{0.9 (P - P')}{W} \quad (6)$$

**METHOD FOR SUGARS.**

The reagents are the same as in the starch method.

For estimating reducing and non-reducing sugars the sample is treated differently, but the solution to be read in the colorimeter has the same limits as mentioned in the starch method. The procedure is as follows:

Transfer a 3 gram sample to a 250 cc. volumetric flask, add 100 cc. of 50% alcohol, and boil on the steam bath for 1 hour. Cool, make up to mark with 95% alcohol, shake well, and filter. Pipet 150 cc. of the filtrate into a 400 cc. beaker and evaporate on the steam bath to about 10 cc. or until only a trace of alcohol is left. Take up with water, transfer to a 100 cc. volumetric flask, and make up to volume. Filter and saturate the filtrate with dry picric acid. Allow to stand 15 minutes, shaking frequently, and again filter. Pipet 3 cc. portions in each of two Nessler tubes such as are used in the starch method, one for reducing sugars and one for total sugars. To the one for reducing sugars add 1 cc. of 22% sodium carbonate solution.

Place both on the steam bath for 20 minutes, together with a tube containing 3 cc. of the standard solution plus 1 cc. of the alkali. After 10 minutes, add 1 cc. of the alkali to the tube for total sugars while still in the bath. Cool, dilute to proper shade, and read. Run a standard with each set of determinations.

Calculate the amount of dextrose and non-reducing sugars as sucrose, thus—

V = Percentage of total sugars,  
 Y = Percentage of reducing sugars,  
 Z = Percentage of non-reducing sugars as sucrose,  
 A = Original volume (250 cc.),  
 H = Volume taken to evaporate (150 cc.),  
 K = Volume to which H is diluted after evaporation (100 cc.),  
 Q = Volume of K taken for reading (3 cc.),  
 S = Final volume of Q,  
 F = Final volume of standard (30 cc.),  
 R<sub>1</sub> = Reading of standard,  
 R<sub>2</sub> = Reading of sample,  
 R<sub>3</sub> = Reading of sample when it is not hydrolyzed,  
 0.0006 = Weight of glucose in grams in 3 cc. of standard,  
 W = Weight of sample taken.

Then—

$$V = \frac{A \times K \times S \times R_1 \times 0.0006 \times 100}{H \times Q \times F \times R_2 \times W}.$$

Simplifying—

$$V = \frac{S \times R_1}{9 \times R_2 \times W}. \quad (7)$$

To calculate reducing sugars, use the same formula, substituting Y for V and R<sub>1</sub> for R<sub>2</sub>. Then—

$$Y = \frac{S \times R}{9 \times R_2 \times W}, \text{ and} \quad (8)$$

$$Z = 0.95 (V - Y). \quad (9)$$

Table 1 shows the results obtained by this method, starting with a bran that had been washed to remove much of the starch, to portions of which a known amount of starch had been added.

TABLE 1.

*Comparison of results obtained on washed bran plus added starch using either taka-diastase or malt solution.*

	WASHED BRAN ALONE	10% STARCH†	15% STARCH‡
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Taka-diastase.....	4.16	10.95	15.26
Theoretical.....	....	12.74	17.04
Taka-diastase.....	5.79	9.86	12.60
Theoretical.....	....	14.21	18.42
Malt solution.....	6.67*	15.22	18.64
Theoretical.....	....	15.00	19.16
Malt solution.....	3.77*	12.02	16.48
Theoretical.....	....	12.39	16.70
Malt solution.....	3.77	12.47	16.45
Theoretical.....	....	12.39	16.70

\*Different lots of bran were used.

†9.0 grams of washed bran was mixed with 1 gram of starch containing 10% of moisture.

‡8.5 grams of washed bran was mixed with 1.5 gram of starch containing 10% of moisture.

Table 1 shows that the amount of starch recovered is closer to the theoretical when using malt solution than when using taka-diaztase.

Table 2 shows the results obtained by this method compared with the results obtained by the copper reduction method on a variety of analyses.

TABLE 2.

*Common feeds analyzed for starch by the copper reduction method and the picric acid method.*

	PICRIC ACID METHOD	COPPER REDUCTION METHOD
	<i>per cent</i>	<i>per cent</i>
Refined cornstarch. . . . .	88.8	88.9
Wheat flour. . . . .	66.9	67.4
Ground whole barley . . . . .	62.7	62.2
Oat middlings. . . . .	48.0	48.3
Wheat bran. . . . .	19.6	19.1
Standard middlings. . . . .	18.3	19.0
Buckwheat middlings . . . . .	17.3	17.5
Peanut meal. . . . .	9.7	9.9
Soy bean meal. . . . .	2.0	2.2
Cottonseed meal. . . . .	0.0	2.6

TABLE 3.

*Factors necessary to convert to other sugars or their hydrated forms<sup>1</sup>.*

CARBOHYDRATE	FORMULA	FACTOR
Rhamnose	$C_6H_{12}O_6$	0.9111
Glucose	$C_6H_{12}O_6 \cdot H_2O$	1.1000
Glucose	$C_6H_{12}O_6$	1.0000
Galactose	$C_6H_{12}O_6$	1.0000
Mannose	$C_6H_{12}O_6$	1.0000
Fructose	$C_6H_{12}O_6$	1.0000
Maltose	$C_{12}H_{22}O_{11} \cdot H_2O$	1.0000
Maltose	$C_{12}H_{22}O_{11}$	0.9500
Lactose	$C_{12}H_{22}O_{11} \cdot H_2O$	1.0000
Lactose	$C_{12}H_{22}O_{11}$	0.9500
Sucrose	$C_{12}H_{22}O_{11}$	0.9500
Raffinose	$C_{18}H_{32}O_{16} \cdot 5H_2O$	1.1000
Raffinose	$C_{18}H_{32}O_{16}$	1.0000

### SUMMARY.

The picric acid colorimetric method hitherto used in biological studies has been successfully applied to the determination of starch or sugar. It eliminates the cumbersome manipulation required by the gravimetric method. One special advantage over other methods, however, is that it can be used to analyze small samples or samples containing small amounts of either. The use of taka-diaztase to saccharify starch was discarded on account of the varying results obtained, but the use of malt produced results that could be checked.

<sup>1</sup> *J. Am. Chem. Soc.*, 1914, 36: 403.

TABLE 4.

*Comparison of picric acid and copper reduction methods in determination of sugar.*

	PICRIC ACID METHOD			COPPER REDUCTION METHOD		
			<i>Average</i>			<i>Average</i>
Alfalfa meal						
Reducing sugars	3.27	3.44	3.36	3.40	3.23	3.32
Non-reducing sugars	1.17	1.21	1.19	1.21	1.27	1.24
Beet pulp						
Reducing sugars	0.39	....	0.39	....	0.35	0.35
Non-reducing sugars	1.34	....	1.34	....	1.35	1.35
Coconut						
Reducing sugars	2.70	2.59	2.65	....	2.19	2.19
Non-reducing sugars	7.36	8.09	7.78	....	7.97	7.97
Corn meal						
Reducing sugars	0.15	0.21	0.18	0.15	0.20	0.18
Non-reducing sugars	1.23	1.17	1.20	1.13	1.12	1.13

A greater variety of examples may be found in A. Bernhard's paper<sup>1</sup>.

Starch and sugar determinations made on a variety of the common feeds compare favorably with those obtained by the copper reduction method.

Since the authors have obtained satisfactory results with this method, they are publishing this paper in the hope that others may try it out and assist in determining its usefulness.

<sup>1</sup> *Sugar.*, 1915, 17: 41.

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## ALFRED W. OGDEN

Alfred W. Ogden, born in Keyport, N. J., August 22, 1869, and for many years a member of the Association of Official Agricultural Chemists, died at his home in East Orange, N. J., January 21, 1924. He married, in 1893, Miss Emma Louisa Barnes of New York City and is survived by his wife and by his three daughters, the Misses Marion and Margaret Ogden of East Orange, and Mrs. H. Seabrook Schanck of Keyport.

Mr. Ogden's higher education was obtained at the Sheffield Scientific School of Yale University. He was graduated from Yale in 1890 with the degree of Ph. B. in chemistry. During part of the years 1889 and 1890 he was connected with the Asbury Park, N. J. Board of Health, and for fourteen years, 1890 to 1904, he was a chemist at the State Agricultural Experiment Station at New Haven, Conn. Most of his experience in the analytical chemistry of foods was acquired during this period, and his activity in this field of work is evidenced by the fact that the name of A. W. Ogden, or A. W. Ogden associated with that of A. L. Winton, E. M. Bailey and others, is found in connection with many of the reports on food products published by the Connecticut Station from 1896 onward.

The New York Laboratory of the Bureau of Chemistry of the United States Department of Agriculture was established in 1904 for the inspection and control of imported foods and drugs entering the port of New York. R. E. Doolittle was made chief of this laboratory and Mr. Ogden, whose appointment as a Food Inspection Chemist in the Department service became effective September 6, 1904, was assigned to his staff. Mr. Ogden had charge of the inspection of imported food products on the floors of the Appraiser's Stores, and his experience at this time and later, after the passage of the Federal food and drugs act, made him an invaluable member of Mr. Doolittle's staff. He was assistant chief of the laboratory for several years and served from time to time as acting chief. These duties took up practically all his time, but his interest in analytical work continued, and he was joint author with Mr. Doolittle of a paper on "Composition of Known Samples of Paprika", published in the September 1908 number of The Journal of the American Chemical Society, and author of an article, entitled "Effect of Storage on Moisture Content of Cloves", printed in the September 1915 number of The American Food Journal. In the official reports to the Secretary of Agriculture upon Mr. Ogden's work in the Department occur such expressions as "splendid training in food analysis", "high efficiency in performance of duties", "good executive", and "one of the most efficient employees of the Bureau of Chemistry".

Sometime after entering the Federal service Mr. Ogden was seriously injured by falling on a slippery pavement in New York City. He never fully recovered from the effects of this accident. His health finally broke, and he found it necessary to ask for a furlough. This request was granted. He was on furlough from January 1, 1918, to June 30, 1921, at which time it became evident that he would never be able to return to work.

Among his associates the memory of the fortitude and cheerfulness with which Mr. Ogden bore the physical disabilities of his later years will perhaps be the most inspiring and lasting memory of the man and his life.

R. W. BALCOM.

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## REPORT OF COMMITTEE ON REVISION OF METHODS OF SOIL ANALYSIS<sup>1</sup>.

The committee's work has been hindered unavoidably by the inability of the former chairman, C. B. Lipman of Berkeley, Calif., to be present at recent meetings of this association. Upon the recent assumption of further executive duties, Lipman tendered his resignation. The present chairman was designated to succeed to the chairmanship, and the vacancy thus caused on the committee was filled by the appointment of A. G. McCall of the University of Maryland.

The problem of revision was handled through correspondence among members of the committee and a number of soil chemists, from whom criticisms were asked. Three of the five members of the committee met in Washington for a full day's session prior to the 1923 meeting of the association and completed the draft that has been submitted to the Committee on Editing Methods of Analysis.

W. H. MACINTIRE, J. A. BIZZELL,  
A. W. BLAIR, A. G. MCCALL.  
R. STEWART,

*Committee on Revision of Methods  
of Soil Analysis.*

### FIRST DAY. MONDAY—MORNING SESSION.

#### REPORT ON WATER.

By J. W. SALE (Bureau of Chemistry, Washington, D. C.), *Referee*.

The referee's work this year included the revision, in cooperation with the Committee on Editing Methods of Analysis, of the methods on water for the new edition of *Methods of Analysis A. O. A. C.*, the collation of methods for the analysis of salt, which have been greatly needed in connection with the control of importations of salt, and a preliminary study of the official method for the determination of hydrogen sulfide in waters.

In July 1923, Heath and Lee<sup>2</sup> recommended that the iodometric method for the determination of hydrogen sulfide in waters be discontinued and that a colorimetric method be used. The iodometric method that these authors used is as follows: "To a measured quantity of the water is added a known excess of a standard solution of iodine. After a short time the excess of iodine is determined by titration with a standard solution of sodium thiosulfate". This method is essentially the same as

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<sup>1</sup> Received too late for publication in Vol. VII, No. 3.

<sup>2</sup> *J. Am. Chem. Soc.*, 1923, 45: 1643.



that given in Standard Methods of Water Analysis, American Public Health Association 1923, p. 58, and Analytical Chemistry, Treadwell-Hall, p. 688. It is so similar to the official method that it was felt that if it gave inaccurate results under certain conditions the official method would also give inaccurate results. Therefore, the work of Heath and Lee was repeated and, in addition, the official method was applied to the synthetic samples. The data obtained are given in Tables 1, 2, and 3. Before discussing these data it should be explained that additional work is necessary before definite conclusions can be drawn as to the accuracy of the official method when the waters to be examined contain large amounts of nitrate, nitrite, carbonate, or organic matter.

C. H. Badger and A. E. Mix of the Water and Beverage Laboratory, Bureau of Chemistry, prepared the synthetic samples and analyzed them.

A solution of hydrogen sulfide in distilled water, containing 50 milligrams or more of hydrogen sulfide per liter, loses strength so rapidly that it was found inadvisable to follow in detail Heath and Lee's procedure, in which they standardized the solution, added the supposedly interfering ingredients, and then determined the content of hydrogen sulfide. In order that the mechanical loss of hydrogen sulfide might not affect the relative values of the results, the samples that did not contain the interfering substances, *i. e.*, nitrate, nitrite, and carbonate, were treated in the same manner as the samples that contained the interfering ingredients. The procedure was as follows:

100 cc. portions of hydrogen sulfide water were siphoned into 100 cc. volumetric flasks from a well-mixed hydrogen-sulfide solution contained in a 2 gallon demijohn. From 2 to 3 cc. of nitrate, nitrite, or carbonate solution, respectively, was added to some of the flasks, and the same quantities of distilled water were added to the other flasks. After being mixed by inverting each flask six times, the contents were poured into 200 cc. volumetric flasks that contained either less or more of an equivalent amount of standard iodine solution, depending upon the method to be employed. The hydrogen sulfide was then determined either by the official A. O. A. C. method or the method used by Heath and Lee. A correction was made for the end point in the A. O. A. C. method.

#### *Effect of nitrate.*

The results given in Table 1, consisting of 41 determinations, show that the addition of nitrate to the amount of 30 milligrams of nitrogen per liter does not materially increase or decrease the amount of hydrogen sulfide found by either method except in two determinations (Nos. 15 and 31), which are obviously abnormal. In other words, considering the instability of the solutions of hydrogen sulfide, the results obtained are in good agreement regardless of whether or not the samples contained added nitrate. These results do not agree, therefore, with those obtained by Heath and Lee, who found that when nitrate was present the results obtained were low.

TABLE 1.  
*Effect of nitrate on determination of hydrogen sulfide.*

METHOD	LABORATORY NUMBER	SAMPLE USED	NITROGEN ADDED AS KNO <sub>3</sub>	H <sub>2</sub> S FOUND	AVERAGE
Experiment 1.					
		cc.	mg.	mg per liter.	mg. per liter
A. O. A. C . . . .	1	115.2	0	68.1	67.5
	2	115	0	67.0	
	3	115	3	67.6	68.2
	4	115	3	68.9	
Experiment 2.					
A. O. A. C. . . . .	5	100	0	60.1	
	6	100	0	58.9	59.5
	7	100	3	60.9	
	8	100	3	61.4	61.1
Experiment 3.					
A. O. A. C. . . . .	9	100	0	28.4	
	10	100	0	29.6	29.0
	11	100	3	29.3	29.3
Experiment 4.					
A. O. A. C. . . . .	12	100	0	25.8	
	13	100	0	26.2	26.0
	14	100	3	26.9	
	15	100	3	31.2*	26.9
Experiment 5.					
A. O. A. C. . . . .	16	100	0	28.1	
	17	100	0	28.2	28.3
	18	100	0	28.6	
	19	100	3	27.9	
	20	100	3	28.4	28.1
Experiment 6.					
A. P. H. A. . . . .	21	100	0	30.3	
	22	100	0	29.4	29.8
	23	100	3	30.3	
	24	100	3	28.6	29.4
Experiment 7.					
A. O. A. C. . . . .	25	100	0	16.8	
	26	100	0	16.6	16.7
	27	100	3	16.8	
	28	100	3	17.0	16.9
Experiment 8.					
A. P. H. A. . . . .	29	100	0	18.4	
	30	100	0	18.4	18.4
	31	100	3	13.7*	
	32	100	3	17.0	17.3
	33	100	3	17.6	
Experiment 9.					
A. P. H. A. . . . .	34	100	0	124.5	
	35	100	0	124.3	124.4
	36	100	3	123.5	
	37	100	3	124.6	124.0
Experiment 10.					
A. O. A. C. . . . .	38	100	0	123.0	
	39	100	0	122.4	122.7
	40	100	3	122.8	
	41	100	3	122.9	122.8

\*Not included in average.

*Effect of nitrite.*

The results of the experiments on the effect of nitrite are contained in Table 2. These results show that 30 milligrams per liter of nitrogen in the form of nitrite does not affect the determination of hydrogen sulfide in a solution containing about 16 milligrams per liter of hydrogen sulfide. However, the same amount of nitrite gave low results (Experiments 13 and 14) when the sample consisted of about 85 milligrams per liter of hydrogen sulfide in distilled water. It appeared that the erratic results might be due to the pH of the solution, which was found to be below 6.0. When the pH value of the solution was increased to 7.4 by the addition of bicarbonate, 30 milligrams per liter of nitrogen in the

TABLE 2.  
*Effect of nitrite on determination of hydrogen sulfide.*

METHOD	LABORATORY NUMBER	SAMPLE USED	NITROGEN ADDED AS NaNO <sub>2</sub>	H <sub>2</sub> S FOUND	AVERAGE
Experiment 11.					
		cc.	mg.	mg. per liter	mg. per liter
A. O. A. C. . . . .	42	100	0	16.3	
	43	100	0	16.4	16.3
	44	100	3	16.1	
	45	100	3	16.3	16.2
Experiment 12.					
A. P. H. A. . . . .	46	100	0	17.6	
	47	100	0	16.7	17.1
	48	100	3	16.7	
	49	100	3	18.2	17.4
Experiment 13.					
A. O. A. C. . . . .	50	100	0	84.2	
	51	100	0	82.2	83.2
	52	100	3	29.2	
	53	100	3	32.9	31.0
Experiment 14.					
A. O. A. C. . . . .	54	100	0	86.9	
	55	100	0	86.1	86.5
	56	100	3	29.1	
	57	100	3	31.7	30.4
Experiment 15.					
A. O. A. C. . . . .	58	100	0	124.9	
	59	100	0	124.5	124.7
	60	100	3	125.4	
	61	100	3	124.7	125.0
Experiment 16.					
A. P. H. A. . . . .	62	100	0	121.9	
	63	100	0	122.3	122.1
	64	100	3	122.4	
	65	100	3	123.1	122.7
Experiment 17.					
A. O. A. C. . . . .	66	100	0	123.9	
	67	100	0	123.6	123.7
	68	100	3	124.5	
	69	100	3	123.7	124.1

form of nitrite was shown to have no material effect by either method, even when the sample contained as much as 120 milligrams per liter of hydrogen sulfide. Heath and Lee reported that nitrite caused high results.

### *Effect of carbonates.*

Carbonates when present to the extent of 390 and 3850 milligrams of carbonate per liter give high results, as shown by Experiments 18, 19, and 20. These results confirm those obtained by Heath and Lee. However, it is a simple matter to convert the carbonate to bicarbonate by titrating the sample with standard acid, using phenolphthalein indicator, and when this is done the results are satisfactory, as shown by Experiment 21.

In view of these preliminary results, no change in the official method is recommended at this time, but the method should be given further study, especially with respect to the effect of pH and organic matter, before final decision is made regarding it. Undoubtedly it will be necessary to recommend a modification of the method when the sample contains large amounts of carbonate.

### METHODS FOR THE ANALYSIS OF SALT.

Methods for the preparation of samples of salt and for the determination of moisture, matters insoluble in water, and matters insoluble in acid were adopted as tentative methods in 1921. As these methods were

TABLE 3.  
*Effect of carbonate on determination of hydrogen sulfide.*

METHOD	LABORATORY NUMBER	SAMPLE USED	CO <sub>2</sub> ADDED AS Na <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> S FOUND	AVERAGE
Experiment 18.					
		cc.	mg.	mg. per liter	mg. per liter
A. P. H. A . . . . .	70	100	0	123.6	
	71	100	0	122.9	123.2
	72	100	39	125.9	
	73	100	39	126.0	125.9
Experiment 19.					
A. O. A. C. . . . . .	74	100	0	117.3	
	75	100	0	117.9	117.6
	76	100	385	179.9	
	77	100	385	197.7	188.8
Experiment 20.					
A. O. A. C. . . . . .	78	100	0	116.1	
	79	100	0	116.1	116.1
	80	100	385	173.9	
	81	100	385	177.6	175.7
Experiment 21.					
A. P. H. A. . . . . .	82	100	0	115.8	
	83	100	0	115.8	115.8
	84	100	385	115.1	
	85	100	385	115.9	115.5

incomplete and inadequate, during the year the referee rewrote and extended them to include the determination of sulfate, calcium, and magnesium, and a method for reporting results. The revised methods, which will be recommended for adoption as tentative methods in place of those adopted in 1921, are not in reality new; they are well recognized methods upon which it has not appeared necessary to do outside collaborative work. They have been in use in the Bureau of Chemistry about a year and have given satisfactory results when used for heavily mineralized waters (except moisture and matters insoluble in water).

These methods follow:

#### PREPARATION OF SAMPLE.

Pass the sample through a 20-mesh sieve, grinding if necessary. Avoid undue grinding so that as much of the sample as possible will be retained on an 80-mesh sieve. Mix sample by quartering and weigh all needed portions as nearly at the same time as possible.

#### MOISTURE.

Place about 10 grams of the sample in a dry, weighed Erlenmeyer flask of about 200 cc. capacity. Weigh flask and sample. Spread sample evenly over the bottom of the flask by shaking gently and insert small funnel in neck. Heat flask and sample for periods of one hour each on a triangle over low, open flame of gas stove at a temperature of about 250° C. until two consecutive weighings agree within 5 milligrams. Shake flask occasionally so that sample will dry evenly. Designate the loss in weight as moisture and express it on a percentage basis.

#### MATTERS INSOLUBLE IN WATER.

Place 10 grams of the sample in a 250 cc. beaker. Add 200 cc. of water at room temperature. Let stand one-half hour, stirring frequently. Filter through a weighed Gooch crucible with asbestos mat dried at 110° C. Transfer the residue to the crucible with the aid of a rubber policeman, using a total of not more than 50 cc. of water. Wash the residue with small portions of water, about 10 portions of 10 cc. each, until 10 cc. of the filtrate shows only a faint opalescence upon addition of a few drops of silver nitrate solution. Dry crucible and contents to constant weight at 110° C. Call the increase in weight of Gooch crucible "matters insoluble in water", and express results in percentage on a moisture-free basis. If the matters insoluble in water exceed 0.1% determine their nature.

#### SULFATE ( $\text{SO}_4$ ), CALCIUM, AND MAGNESIUM.

##### PREPARATION OF SOLUTION.

Weigh about 20 grams of the sample and dissolve in 150 cc. of water and 50 cc. of hydrochloric acid (sp. gr. 1.18) in a 400 cc. beaker. Cover the beaker, heat to boiling, and continue boiling gently for 10 minutes. Filter through paper filter and wash residue with small amounts of hot water until the filtrate is free from chloride. Unite filtrate and washings, cool, and make up to 500 cc. volume. (Solution A).

##### SULFATE ( $\text{SO}_4$ ).

Place 250 cc. of Solution A in a 400 cc. beaker of resistant glass, heat to boiling, and add a slight excess of a hot 10 per cent barium chloride solution drop by drop while stirring. Concentrate by heating gently and finally evaporate to dryness on the steam bath. Facilitate removal of the free acid by stirring the partly dry residue. Wash the precipitate by decantation with small quantities of hot water, finally transferring the precipitate to the close-grained filter paper with the aid of a rubber policeman and

stream of hot water. Wash the precipitate on the filter until the filtrate is free from chloride. Test the filtrate for the presence of sulfate. Dry and ignite the filter and precipitate over a Bunsen flame. Report the percentage of sulfate ( $\text{SO}_4$ ) on a moisture-free basis.

#### CALCIUM.

Place the remainder of Solution A in a 400 cc. beaker of resistant glass. Add an excess of 10 per cent oxalic acid solution (10 cc. of the reagent usually will be sufficient). Add a few drops of methyl orange solution and neutralize while hot by adding strong ammonia water drop by drop, stirring constantly. Add about 1 cc. of excess strong ammonia water, stir, and let stand in a warm place for 3 hours. Decant the supernatant liquid through a filter, reserving the filtrate for the determination of magnesium. Test the filtrate for calcium with ammonium oxalate solution. Wash the precipitate in a beaker once with 10 cc. of 1 per cent ammonium oxalate solution, decanting through filter paper. Combine filtrate and washings. Dissolve the precipitate in a beaker and on the filter with hot, dilute hydrochloric acid, dilute to 100 cc., add a little oxalic acid, and precipitate as before. After standing 3 hours, filter, wash with ammonium oxalate solution as before, reserving the filtrate and washings. Transfer the precipitate to the filter, dry, ignite, and heat over a blast lamp to constant weight. Report as percentage of calcium, moisture-free basis.

#### MAGNESIUM.

Combine filtrates and washings from the calcium determination and concentrate if necessary, by boiling gently, to a volume of about 150 cc. Add about 2 grams of diammonium hydrogen phosphate and sufficient hydrochloric acid to clear the solution when the ammonium phosphate is all dissolved. Disodium hydrogen phosphate or sodium ammonium hydrogen phosphate may be used instead of the diammonium hydrogen phosphate. When cold, make slightly alkaline with ammonium hydroxide, stirring constantly. Add 1 to 2 cc. excess of ammonium hydroxide and allow to stand about 12 hours. Filter off the supernatant liquid and wash 3 or 4 times by decantation with a solution of 2.5 per cent ammonium hydroxide. Dissolve the precipitate in hydrochloric acid, dilute to about 75 cc., add a little diammonium hydrogen phosphate and precipitate with ammonium hydroxide as before. Allow to stand 6-12 hours, filter, wash free from chlorides, ignite, heat over a blast lamp, and weigh as magnesium pyrophosphate. Calculate to percentage of magnesium on a moisture-free basis.

#### METHOD OF REPORTING RESULTS.

(In the absence of added drying agents such as magnesium carbonate, calcium phosphate, etc.)

Calculate the sulfate to calcium sulfate, and the unused calcium to calcium chloride, unless the sulfate in the sample exceeds the quantity necessary to combine with the calcium, in which case calculate the calcium to calcium sulfate and the unused sulfate first to magnesium sulfate and the remaining sulfate, if any, to sodium sulfate. Calculate unused magnesium to magnesium chloride. Add together the percentages of chlorides of calcium and magnesium.

Report on a moisture-free basis the percentage of matters insoluble in water, of sulfate, of calcium, of magnesium, of calcium sulfate and of chlorides of calcium and magnesium. Report also the results of the qualitative examination of matters insoluble in water, if the amount exceeds 0.1% on a moisture-free basis.

#### METHOD FOR THE DETERMINATION OF BROMINE IN THE PRESENCE OF CHLORINE AND IODINE.

This method was thoroughly studied by the Referee on Water and his co-workers in 1920, and published in *The Journal*<sup>1</sup>. It was not recom-

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 29.

mended for adoption at that time because the results obtained were slightly low, although it was recognized as the best method for bromine in the presence of chlorine and iodine that had been published. Further consideration of the method seems to warrant its adoption by the association as a tentative method.

#### RECOMMENDATIONS.

It is recommended—

(1) That the title of Chapter III of the *Book of Methods* be changed from "Waters" to "Waters, Brine, and Salt". This recommendation is in accord with Recommendation 6<sup>1</sup>, submitted in 1919, "that the methods on water be extended to cover the examination of allied products, such as brine and salt".

(2) That the method for bromine in the presence of chlorine and iodine, as published in *The Journal*, be adopted as a tentative method.

(3) That the method for free and albuminoid ammonia (in samples containing sulfide)<sup>2</sup> be adopted as official. (First action was taken in 1919<sup>3</sup>.)

(4) That the method for salt, as given in this report, be adopted as a tentative method.

(5) That the methods for salt that were published previously<sup>4</sup> be dropped.

#### REPORT ON TANNING MATERIALS AND LEATHER.

By F. P. VEITCH (Bureau of Chemistry, Washington, D. C.), *Referee*.

No changes have been made in the tentative methods of the association for the analysis of tanning materials and leather for more than ten years. During that time considerable progress has been made in the development of methods, more especially for the analysis of leather, and since it is proposed to revise and reprint the methods of the association it has been deemed highly desirable to bring those for the analysis of tanning materials and leather up to date and in agreement with the best known methods for the examination of these products.

To this end, the referee has gone carefully over the methods and rewritten them. As submitted to the Committee on Methods of Analysis they are practically identical with the methods of the American Leather Chemists Association and in close agreement with those of the Association of Leather Trades Chemists of England, France, and Belgium.

These methods have been developed after careful cooperative study, participated in by members of this association and approved by them.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 4: 566.

<sup>2</sup> *Ibid.*, 387.

<sup>3</sup> *Ibid.*, 566.

<sup>4</sup> *Ibid.*, 1922, 5: 384.

They are the best now known for the respective materials; in fact they are quite satisfactory, with the exception of the methods for the determination of tannin and ether extract. The latter should more adequately cover fats, oils, waxes, soaps, and oxidized products of oils and fats.

#### RECOMMENDATIONS.

It is recommended—

- (1) That the proposed changes in the tentative methods of the association for the analysis of tanning materials and leather be adopted.
- (2) That a study be made of the method for the determination of tannin in tanning materials and leather with a view to working out a more accurate method.
- (3) That work be continued on the study of solvents for the determination of grease, soap, and oxidized oils and fats in leather.

#### REPORT ON INSECTICIDES AND FUNGICIDES.

By J. J. T. GRAHAM (Bureau of Chemistry, Washington, D. C.). *Referee.*

The association, at its last meeting, directed that the work on insecticides and fungicides for 1923 be a study of methods for the analysis of dusting mixtures. These preparations usually consist of two or more of the following substances: lead arsenate, calcium arsenate, Paris green, Bordeaux mixture, sulfur, lime, calcium sulfate, kaolin, tobacco powder, and nicotine solution. Since the compositions of these insecticides are so diverse, the referee decided it would be the better plan to limit the work to definite groups of these materials than to take up the subject in a general way. Considering the active ingredients of these mixtures, it was found that the association has satisfactory methods for nicotine in any mixture of the materials named. There are also satisfactory methods for total arsenic, copper, and lead in the various Bordeaux-arsenical combinations. It seemed, therefore, that before proceeding with the work it would be well to ascertain the methods in use and the difficulties that had been experienced in the various laboratories in the analysis of this class of products. The following letter was therefore sent to nineteen laboratories.:

The Association of Official Agricultural Chemists at the last meeting directed that the work on insecticides and fungicides for 1923 be a study of methods for the analysis of dusting mixtures that are now being used in large quantities in place of the wet sprays.

In taking up this work I think it advisable to ascertain what methods are now in use in the various laboratories charged with the enforcement of insecticide laws. I would therefore be glad to receive copies of any methods you are using for the analysis of these insecticides, and also any suggestions you may have to offer.



Only two of the replies gave suggestions for work, and one of these related to insecticides other than dusting mixtures. The author of the suggestion for work on dusting mixtures cited the fact that his laboratory had obtained high values for arsenic in samples containing a large percentage of sulfur and advised that work be done on the determination of arsenic in mixtures containing free sulfur. As analysts in the Insecticide and Fungicide Laboratory of the Bureau of Chemistry had also experienced difficulty in determining arsenic in such mixtures, the referee acted on this suggestion.

Preliminary work was undertaken with samples containing 90 per cent of sulfur, the other 10 per cent being either calcium arsenate or lead arsenate. Arsenic was determined by the official distillation method<sup>1</sup>. Sulfur distilled with the arsenic, causing a cloudy distillate, but the results checked the calculated values fairly well, showing that elemental sulfur is not the cause of high results for arsenic oxide in samples of this nature. This was further verified by distilling the following combinations of reagents: sulfur and hydrochloric acid; sulfur, cuprous chloride, and hydrochloric acid; and sulfur, calcium arsenate, and hydrochloric acid. The titrations of aliquots of these distillates were equivalent in each case to the blank.

Since it was found that the high results for arsenic oxide occasionally obtained on samples of this kind are not caused by elemental sulfur, it was necessary to seek some other source of error. As many of these samples contain free lime, it was considered that some of it might react with the sulfur to form sulfides. Following this idea, a sample was prepared containing 89 per cent of sulfur, 10 per cent of calcium arsenate, and 1 per cent of "dry lime sulfur", a commercial product prepared by drying in vacuo lime sulfur solution in the presence of sugar.

Analysis of this sample by the official distillation method gave incorrect results, the error being as great as 6 per cent of the arsenic present.

The referee was unable to find in the literature reference to any method that he considered applicable to the determination of arsenic under the foregoing conditions. A. C. Nothstine of the Insecticide and Fungicide Laboratory of the Bureau of Chemistry suggested a method that had given good results on such samples, and this method, slightly modified by the referee, was used in the collaborative work this year.

#### PREPARATION OF SAMPLES.

*Sample No. 1.*—Fifty parts of commercial calcium arsenate, 25 parts of flowers of sulfur, and 25 parts of commercial dry lime sulfur were passed through a No. 40 sieve and thoroughly mixed.

The calculated value for arsenic oxide in this sample is 19.86 per cent.

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<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 54.

*Sample No. 2.*—Twenty-five parts of commercial calcium arsenate, 25 parts of flowers of sulfur, and 50 parts of commercial dry lime sulfur were mixed in the same manner as in Sample No. 1. The calculated value for arsenic oxide in this sample is 9.93 per cent.

After preliminary work on these samples by the referee they were sent to the collaborators with the following directions:

METHOD FOR THE DETERMINATION OF ARSENIC IN THE PRESENCE  
OF SULFIDES, SULFITES, THIOSULFATES, OR LARGE AMOUNTS  
OF SULFUR.

TOTAL ARSENIC.

REAGENTS.

- (a) *Starch indicator.*—Prepare as directed under Paris green<sup>1</sup>.
- (b) *Standard arsenious oxide solution.*—Prepare as directed under Paris green.
- (c) *Standard iodine solution.*—Prepare as directed under Paris green.

DETERMINATION.

*Proposed method.*

Weigh 2.0 grams of the sample and transfer to a distillation flask. Add a solution of 5-8 grams of cuprous chloride in 100 cc. of concentrated hydrochloric acid. Shake the flask to bring the sample completely into contact with the acid solution and to expel hydrogen sulfide. When the reaction has stopped, close the flask, connect to the condenser, and distil as in the official distillation method<sup>2</sup>. Make the distillate to volume in a liter flask, mix thoroughly, and transfer a 200 cc. aliquot to a 400 cc. Pyrex beaker or porcelain casserole. Add 10 cc. of concentrated nitric acid and 5 cc. of sulfuric acid and evaporate to a sirupy consistency on the steam bath and then on a hot plate until the appearance of white fumes of sulfuric acid. Cool and transfer to a 500 cc. Erlenmeyer flask. If the quantity of sulfuric acid has been appreciably lessened by fuming, add sufficient to bring it up to 5 cc. Dilute to 100-150 cc., add 1.5 grams of potassium iodide, and boil until the volume is reduced to about 40 cc. Cool the solution under running water, dilute to 150-200 cc., and exactly remove any free iodine in the solution with a few drops of approximately 0.05 normal sodium thiosulfate. Nearly neutralize the sulfuric acid with a solution of sodium hydroxide (40 grams in 100 cc. of water) and finish the neutralization with sodium bicarbonate, adding 4-5 grams in excess. Titrate with standard iodine solution, using starch as an indicator.

*Official distillation method.*

Make analysis of each sample by the official distillation method, following the method exactly.

Reports from eight laboratories are given in Table 1.

COMMENTS BY ANALYSTS.

*E. L. Green.*—It is obvious that the second (proposed) method gives more consistent indications especially with samples low in arsenic. Also in our work some sort of solid came over, and an effort was made to apportion this evenly among the several aliquot

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 53.

<sup>2</sup> *Ibid.*, 54.

TABLE 1.  
*Cooperative results on total arsenic, calculated as arsenic oxide.*

ANALYST	SAMPLE No. 1		SAMPLE No. 2	
	PROPOSED METHOD	OFFICIAL DISTILLATION METHOD	PROPOSED METHOD	OFFICIAL DISTILLATION METHOD
J. J. T. Graham . . . . .	<i>per cent</i> 19.69 19.69 19.76 19.76	<i>per cent</i> 20.33 20.04 20.33 ....	<i>per cent</i> 9.88 9.91 .... ....	<i>per cent</i> 10.84 11.08 11.27 ....
Average . . . . .	19.73	20.23	9.90	11.06
E. L. Green, Agricultural Experiment Station, Pullman, Wash.	19.73 19.40 19.76 ... ... ...	18.66 19.50 19.09 18.88 ... ...	9.63 10.00 10.09 .... .... ...	9.25 10.12 9.56 10.63 11.67 8.78
Average . . . . .	19.63	19.03	9.91	10.00
A. P. Kerr, Agricultural Experiment Station, Baton Rouge, La.	19.34 19.41	20.16 20.03	10.00 9.86	10.69 10.56
Average . . . . .	19.38	20.10	9.93	10.63
Errol Middleton, Agricultural and Mechanical College, College Station, Texas	18.61 18.52	30.69 30.96	9.62 9.55	17.43 17.43
Average . . . . .	18.57	30.83	9.59	17.43
W. G. Marshall, Department of Agriculture, Sacramento, Calif.	19.54	15.31	9.71	9.99
R. H. Robinson, Agricultural Experiment Station, Corvallis, Ore.	19.33 19.39 19.33 19.30 ... ... ... ...	19.26 19.90 19.61 19.47 ... ... ... ...	9.60 9.63 9.63 9.60 ... ... ... ...	9.76 10.41 8.53 8.87 8.95 9.70 10.11 9.33
Average . . . . .	19.34	19.56	9.62	9.46
E. R. Tobey, Agricultural Experiment Station, Orono, Maine	19.96 19.86	19.75 20.56	10.11 9.97	11.27 10.57
Average . . . . .	19.91	20.16	10.04	10.92
O. B. Winter, Agricultural Experiment Station, East Lansing, Mich.	19.49 19.73 19.49 18.99	20.74 20.65 ... ...	10.28 10.05 ... ...	11.73 11.73 ... ...
Average . . . . .	19.43	20.70	10.17	11.73
S. H. Wilson, Department of Agriculture, Atlanta, Ga.	18.96	19.93	9.22	11.39
General Average . . . . .	19.44	20.66	9.81	10.80
Calculated value . . . . .	19.86	19.86	9.93	9.93
Average deviation from calculated value . . . . .	0.39	1.68	0.23	1.36
Average deviation from mean . . . . .	0.28	1.94	0.22	1.32
Maximum deviation from mean . . . . .	0.92	10.30	0.59	6.63

portions of the distillate. It was felt that some variation in the values obtained with different portions of the same distillate might be due to the presence of this solid.

*R. H. Robinson.*—As indicated by duplicate determinations of aliquots from the same distillation it is apparent that the official method can not be used for this class of material. It was observed that the amount of sulfur obtained in the distillate and the state that this assumed in the receiving flask, \* \* \* was influenced by the degree of heat applied to the distillation flask and the speed with which it was distilled. No trouble was experienced in obtaining check results by the use of the revised method.

*S. H. Wilson:*

*Sample No. 1.*—Small amount of sulfur and some hydrogen sulfide distilled over by both methods.

*Sample No. 2.*—Large amounts of sulfur and some hydrogen sulfide distilled over by both methods.

*Proposed method.*—Determinations run through simultaneously in duplicate check nicely, but determinations made at various times do not check well. The results of proposed method are averages of eight determinations.

## DISCUSSION.

The samples used in the cooperative work this year contained much greater quantities of sulfides than are likely to be encountered in commercial samples. The referee made them up to represent extreme cases so that the method, if satisfactory for them, would certainly be accurate for samples containing smaller amounts of these compounds.

In the official method evolution of hydrogen sulfide gas occurs when the acid is added. Some of this gas is distilled with the arsenic chloride and forms arsenic sulfide in the receptors. This is prevented in the proposed method by dissolving the cuprous chloride in the hydrochloric acid before introduction into the flask. In this condition it reacts more readily with the hydrogen sulfide to form copper sulfide and thus prevents the formation of arsenic sulfide in the distillate. (One collaborator reported that he obtained some hydrogen sulfide in the distillate.) Errors due to volatile reducing substances are prevented in the proposed method by oxidation of the distillate with nitric and sulfuric acids.

An examination of the figures in Table 1 shows conclusively that the official distillation method gives inaccurate analyses of samples of this character. The tendency of most of the analysts was to obtain high results. The results by the proposed method are more consistent, and in general they check the calculated values more closely than those by the official distillation method. When the unfavorable condition under which arsenic oxide must be determined in these samples is taken into account, the results are considered good. Some of the variation in the results by the different collaborators may be due to differences in the composition of the samples, as it is difficult to prepare a uniform mixture using these three ingredients. The referee believes that this method will give good results on many samples that can not be accu-

rately analyzed by the official distillation method. It is therefore recommended that it be adopted as a tentative method for the determination of arsenic oxide in the presence of sulfides, sulfites, thiosulfates, or large amounts of sulfur.

#### SUGGESTIONS FOR FUTURE WORK.

The time consumed in making a determination of water-soluble arsenic by the association method prohibits its use for factory control in the manufacture of insecticides. It is desirable that these products be tested in the factory by the same method that is to be used later in their inspection. The referee suggests that a study be made with the view to obtaining a method that will consume less time and give results comparable to the present method.

The association has adopted no methods for the analysis of oil emulsions, which are extensively used at the present time. This should be the subject of early cooperative study.

Miscible oils also are used to a large extent in certain sections of the country, and methods for the analysis of this class of insecticides should be studied.

#### REVISION OF CHAPTER VI OF THE BOOK OF METHODS<sup>1</sup>.

At the request of the chairman of the Committee on Editing Methods of Analysis, the referee has reviewed Chapter VI of the Book of Methods and suggests the following changes:

In most of the arsenic methods the directions for the determinations begin with such expressions as "Weigh an amount of the sample equal to the arsenious oxide equivalent of 250 cc. of the standard iodine solution". This wording is often confusing to chemists unfamiliar with the methods. In addition it has been found that most chemists prefer to disregard these factor weights, and it is therefore suggested that they be eliminated from the chapter.

In the apparatus for the distillation of arsenious chloride, paragraph 4, it has been found that the third receiving flask is unnecessary and that it is more convenient to have both the first and second receiving flasks of 500 cc. capacity. It has also been found that water circulating through the pan is permissible as a cooling agent. It is suggested that these changes be made.

Paragraphs 7 and 8 are similar and should be combined into one paragraph.

The method for copper in Bordeaux mixture with Paris green, given in paragraph 47, is not satisfactory, and the referee suggests that it be changed to read as follows:

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 53-59.

Dissolve 2 grams of the powdered sample in a 150 cc. beaker with 5 cc. of concentrated nitric acid, add 25 cc. of a 3% solution of hydrogen peroxide and warm on a steam bath for 5-10 minutes. Dilute to about 100 cc. with hydrogen peroxide solution and electrolyze, using a weighed gauze cathode, a rotating paddle anode, and a current of 2 to 3 amperes. At the end of about 20 minutes add 15-20 cc. more of hydrogen peroxide solution. After the deposition of all the copper, which should not require more than 45 minutes, wash the deposit with water by siphoning, rinse with alcohol, dry for a few minutes in an oven, weigh, and calculate the percentage of copper. (Do not pass the current for more than 5-10 minutes after all copper is deposited without adding more of the hydrogen peroxide solution.)

In the analysis of formaldehyde solutions, Brom-Thymol Blue is a better indicator than litmus and paragraph 69 should be amended to permit its use as an optional indicator.

When the directions for the determination of sulfate sulfur, paragraph 81, are followed the solution is very difficult to filter owing to the presence of starch. If the following procedure is followed the starch is hydrolyzed and causes no further trouble.

Slightly acidify the solution from the determination of thiosulfate sulfur, 76, with hydrochloric acid, heat to boiling and precipitate with 10% barium chloride solution; boil for 30 minutes, allow to stand overnight, filter, ignite, and weigh. Calculate the sulfur from the weight of barium sulfate and report as sulfate sulfur.

#### RECOMMENDATIONS.

It is recommended—

(1) That the hydrazine distillation method for total arsenic, as given in the referee's report for 1921<sup>1</sup>, be adopted as an official method.

(2) That the method for the determination of total arsenic oxide in the presence of sulfides, sulfites, and thiosulfates, or large amounts of sulfur, be adopted as a tentative method.

(The following recommendations refer to Chapter VI of the *Book of Methods* with the exceptions noted.)

(3) That the following methods be grouped under the heading "General Methods" and placed at the beginning of the chapter:

Preparation of the Sample; Moisture; Copper Chloride and Hydrazine Distillation Methods for Total Arsenic, including both iodine and bromate titrations; Water-soluble Arsenic; and the General Procedure for the Analysis of a Product containing Arsenic, Antimony, Lead, Copper, Zinc, Iron, Calcium, Magnesium, etc.

(4) That directions for the use of factor weights be discontinued, and that statements of the approximate weights of sample to be used be incorporated in their stead.

(5) That paragraph 4 be changed as described previously in this report.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 402.

(6) That paragraphs 7 and 8 be combined in one method, and be adopted as an official method.

(7) That paragraph 47 be changed as previously described in this report and be adopted as an official method.

(8) That in the determination of formaldehyde in formaldehyde solutions, paragraphs 68 and 69, the method be amended to permit the use of Brom-Thymol Blue as an optional indicator.

(9) That paragraph 81 be changed as previously described in this report.

(10) That the following tentative methods be adopted as official methods:

Paragraph 1.—Preparation of Sample.

Paragraph 2.—Moisture in Paris Green.

Paragraphs 11 and 12.—Water-soluble Arsenious Oxide in Paris Green.

Paragraph 15.—Moisture in London Purple.

Paragraph 20.—Water-soluble Arsenious Oxide in London Purple.

Paragraphs 21 and 22.—Water-soluble Arsenic Oxide in London Purple.

Paragraph 23.—Moisture in Lead Arsenate.

Paragraphs 25 and 26.—Total Lead Oxide in Lead Arsenate.

Paragraphs 30 and 31.—Water-soluble Arsenic in Lead Arsenate.

Paragraphs 32 and 33.—Total Arsenious Oxide in Lead Arsenate.

<sup>1</sup>.—Total Arsenious Oxide in Magnesium Arsenate.

Paragraph 38.—Total Arsenious Oxide in Zinc Arsenite.

Paragraph 45.—Moisture in Bordeaux Mixture with Paris Green.

Paragraphs 50 and 51.—Total Arsenious Oxide in Bordeaux Mixture with Paris Green.

Paragraph 52.—Water-soluble Arsenious Oxide in Bordeaux Mixture with Paris Green.

Paragraph 58.—Water-soluble Arsenic in Bordeaux Mixture with Lead Arsenate.

(11) That the following tentative methods be dropped:

<sup>2</sup>.—Total Arsenic in London Purple.

<sup>1</sup>.—Total Arsenious Oxide in Calcium Arsenate.

Paragraph 48.—Method II for Copper in Bordeaux Mixture with Paris Green.

Paragraph 55.—Copper in Bordeaux Mixture with Lead Arsenate.

Paragraph 56.—Lead Oxide in Bordeaux Mixture with Lead Arsenate.

<sup>1</sup> Assoc. Official Agr. Chemists, Methods, 1920, 59; J. Assoc. Official Agr. Chemists, 1921, 4: 403.

<sup>2</sup> J. Assoc. Official Agr. Chemists, 1921, 5: 50.

## A RAPID METHOD FOR THE DETERMINATION OF LEAD AND ARSENIC IN LEAD ARSENATE<sup>1</sup>.

By C. C. HEDGES and W. A. STONE (Agricultural and Mechanical College of Texas, College Station, Tex.).

According to the methods of analysis of the A. O. A. C., lead in lead arsenate is determined by the official lead chromate and tentative lead sulfate methods, and arsenic is determined by the distillation and potassium iodide methods, both official. The lead chromate may retain some lead arsenate, in which case slightly high results will be obtained, and the lead sulfate method is not applicable in the presence of calcium. Last year Graham and Smith<sup>2</sup>, of the Bureau of Chemistry, published the hydrazine sulfate distillation method for total arsenic; this method gives excellent results. No method is given, however, for the determination of both lead and arsenic on the same weighed sample.

The object of this investigation was to combine the lead sulfate and potassium iodide methods by determining the lead on the dissolved sample direct, without an evaporation, and the arsenic on the filtrate and washings, saving, thereby, about one-third the time required for the analysis.

### *Comparative Results.*

SAMPLE NO.	LEAD OXIDE BY LEAD CHROMATE METHOD (Official)	LEAD OXIDE BY LEAD SULFATE METHOD (Modified)	ARSENIC OXIDE BY HYDRAZINE SULFATE METHOD	ARSENIC OXIDE BY POTASSIUM IODIDE METHOD (Modified)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A	64.33 64.32	64.20 64.18	31.88 31.90	31.90 31.85
B	70.60 70.64	70.61 70.63	25.96 25.95	25.93 25.95
C	63.99 64.03	63.99 64.04	32.41 32.42	32.45 32.41
D	62.20 62.21	62.18 62.14	30.56 30.53	30.46 30.50
E	65.20 65.22	65.21 65.22	30.56 30.56	30.44 30.56
F	69.79 69.79	69.81 69.80	27.02 27.07	26.90 26.92
G	64.21 64.13	63.95 63.87	31.52 31.52	31.60 31.53

<sup>1</sup> Presented by W. A. Stone.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1922, 14: 207.



The procedure was as follows:

(1) *Lead determination*.—Weigh out 0.7360 gram of the dry powdered sample, transfer to a 250 cc. beaker, add 20 cc. of 6N sulfuric acid, boil gently with constant stirring for ten minutes, add 50 cc. of water and 100 cc. of 95 per cent alcohol, and then proceed as in the official method<sup>1</sup>. This method is not applicable in the presence of calcium or insoluble inert material.

(2) *Arsenic determination*.—Add 2 grams of potassium iodide to the lead sulfate filtrate and washing and proceed as in the official potassium iodide method<sup>1</sup>, but use 0.1N instead of 0.05N iodine for the titration. (If preferred, however, the filtrate and washings may be diluted to 250 cc., an aliquot part taken, and the titration made with 0.05N iodine.)

All samples were analyzed for lead by the lead chromate and lead sulfate methods, and for arsenic by the hydrazine sulfate and potassium iodide methods. The lead sulfate and potassium iodide methods were modified according to the above procedure. The results obtained are shown in the table.

## A QUICK METHOD FOR DETERMINING WATER-SOLUBLE ARSENIC IN LEAD ARSENATE AND ZINC ARSENITE.

By R. C. ROARK (Insecticide and Fungicide Laboratory, Miscellaneous Division, Bureau of Chemistry, Washington, D. C.).

The purpose of this paper is to present to the association a method for the determination of water-soluble arsenic in lead arsenate and zinc arsenite that has been shown to yield results comparable to those obtained by the present official method, with the expenditure of much less time.

### HISTORICAL.

#### LEAD ARSENATE.

Methods for the analysis of lead arsenate were first proposed by Haywood<sup>2</sup> in 1906. It was suggested in these methods that water-soluble arsenic oxide be extracted by placing 2 grams of the lead arsenate paste in a flask with 2,000 cc. of carbon-dioxide-free distilled water and allowing to stand 10 days, shaking eight times each day. In 1907 the association adopted this method<sup>3</sup> as provisional and recommended its further study. Results by different analysts with this method were presented to the association in 1909, with a recommendation for further study by the referee on insecticides, McDonnell<sup>4</sup>. In 1910 very concordant results were obtained by the cooperating chemists in determining water-soluble arsenic oxide in a mixture of lead arsenate, calcium arse-

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 58.

<sup>2</sup> U. S. Bur. Chem. Bull. 105, 165.

<sup>3</sup> *Ibid.*, 107, rev., 165.

<sup>4</sup> *Ibid.*, 132, 42.

nate, calcium carbonate, and sodium arsenate by the 10-day extraction method. McDonnell<sup>1</sup> also presented results showing that a 2-day extraction yielded results almost as high as extractions extending over 4, 6, 8, 10, or 16 days, and recommended that the method for soluble arsenic in lead arsenate be further studied as regards the time of standing necessary for the complete solution of soluble arsenic. In 1911 additional results were reported on methods for determining water-soluble arsenic in lead arsenate. The average of the results obtained for water-soluble arsenic oxide in one sample of lead arsenate by nine analysts was 0.83 per cent by the 10-day and 0.59 per cent by the one-day extraction method. For another sample of lead arsenate the respective averages were 0.17 per cent and 0.10 per cent. The recommendation of the referee on insecticides, McDonnell<sup>2</sup>, was "That the method for water-soluble arsenic oxide in lead arsenate be further studied as regards time of standing for the solution of soluble arsenic and the effect of different temperatures thereon".

In 1912 Curry and Smith<sup>3</sup> published a paper giving the results of tests to determine water-soluble arsenic in lead arsenate. They found that if 2 grams of the material in paste form were added to 500 cc. of water kept at 20°C. in a thermostat and continuously stirred for 18 hours results were obtained that, while slightly lower, agreed very well with those obtained by the 10-day extraction method used by this association at that time. They suggested a deduction of 0.15 per cent arsenic pentoxide from the results in order to correct for the solubility of lead arsenate—the soluble arsenic pentoxide remaining representing the soluble "free" arsenic.

In 1912 the following methods for the extraction of water-soluble arsenic in lead arsenate were presented to the association:

(1) Weigh to 0.01 gram about 2 grams of paste, place in a tightly stoppered bottle with 200 cc. of carbon-dioxide-free water per gram; put into a mechanical shaker and shake for 3 hours; let stand 2 hours and filter. (2) Same as (1) except that the bottles should be placed at some convenient place in the laboratory and shaken every half hour, or as often as possible during a working day. Let stand overnight and filter.

Results by 3 analysts on a sample of lead arsenate paste by these two methods checked very closely, and the referee, Averitt<sup>4</sup>, recommended their adoption as provisional by the association.

In 1913 no work was done on methods for water-soluble arsenic, but the referee, Averitt<sup>5</sup>, made the following recommendation:

It is recommended that the following method of digestion for water-soluble arsenic in lead arsenate be made a provisional method, and that the present provisional method

<sup>1</sup> U. S. Bur. Chem. Bull., 137; 36.

<sup>2</sup> *Ibid.*, 152, 68.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1912, 4: 198.

<sup>4</sup> U. S. Bur. Chem. Bull. 162, 27.

<sup>5</sup> *J. Assoc. Official Agr. Chemists*, 1915, 1: 59.

of digestion be dropped: *Water-soluble arsenic*.—Weigh to 0.01 gram about 4 grams of paste; place in a tightly stoppered flask or bottle with 250 cc. of freshly boiled and cooled distilled water per gram and keep at 32°C. for 24 hours, shaking well every hour during the working day (eight times in all) and filtering at the end of 24 hours.

In 1914 cooperative work was done on the 24-hour extraction method for water-soluble arsenic in lead arsenate-Bordeaux combinations. The results were good, and the referee, Roark<sup>1</sup>, recommended the adoption of the method as applied to this material as a provisional method and in 1915<sup>2</sup> as a tentative method. The 24-hour extraction method, including the use of carbon-dioxide-free water, was adopted by this association in 1916 as tentative for the determination of water-soluble arsenic in lead arsenate and lead arsenate-Bordeaux combinations. It has been published in the *Book of Methods*<sup>3</sup>.

Robinson and Tartar<sup>4</sup>, in 1915, described what they designate the "Oregon Station Method" for the extraction of water-soluble arsenic in lead arsenate. This method directed that the soluble arsenic be extracted by placing a convenient quantity (4 to 6 grams) of the sample on a No. 590 S. & S. filter paper and washing with hot distilled water free from carbon dioxide and ammonia till about 1 liter of filtrate was obtained. Results by this method were slightly higher than those obtained by the 10-day extraction method.

Gray and Christie<sup>5</sup>, in 1916, stated that the Colby method for the determination of water-soluble arsenic in Paris Green had been used to a considerable extent in California in the examination of samples of commercial lead arsenate. In the Colby method 0.5 gram of dry powder is placed in a flask with 100 cc. of carbon-dioxide-free water, set in a warm place, and shaken every hour during the working day. After standing overnight the water is poured off, and a fresh 100 cc. portion is added and treated as before on the second and third days. The combined leachings are then filtered and arsenic is determined in the filtrate in the usual manner.

Gray and Christie also describe a method used by them as follows:

A 0.5 gram portion of dry powder is placed in a 500 cc. Erlenmeyer flask, 200 cc. distilled water added and boiled briskly for 10 minutes. If the liquid is cloudy or the sample does not settle readily, digest on the steam bath an hour or two or until the supernatant liquid is clear. Filter through a No. 590 S. & S. filter paper, wash with hot water, and determine arsenic in the filtrate by the potassium iodide reduction method.

Tested on samples of commercial lead arsenate pastes representative of the products of different manufacturers, the Gray and Christie method yielded higher results than the A. O. A. C. 10-day method—in some

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1915, 1: 435.

<sup>2</sup> *Ibid.*, 1917, 3: 157.

<sup>3</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 59.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1915, 7: 499.

<sup>5</sup> *Ibid.*, 1916, 8: 1109.

cases almost twice as much (2.17 per cent as against 1.26 per cent for example). Gray and Christie also stated that no difference in the results were observed whether boiled or unboiled distilled water was used for making the extraction.

In 1917 Scholz and Waldstein<sup>1</sup> published a method used by them for factory control in the manufacture of lead arsenate. The procedure was as follows:

Place 0.5 gram dry powder in a 250 cc. volumetric flask, add 200 cc. recently boiled distilled water, and boil vigorously for 3 to 5 minutes. After cooling and making to volume, filter the solution and determine arsenic in an aliquot by the potassium iodide reduction method.

Tested on a number of lead arsenates, representing practically every known commercial method of manufacture, this method yielded results very slightly higher than those obtained by the A. O. A. C. 24-hour method.

In 1917 Scott<sup>2</sup> published the following method for the determination of soluble arsenic in lead arsenate.

Two grams of the paste is digested with 1,000 cc. of water at 90° F. for 5 minutes, in a graduated 1,000 cc. flask. An aliquot portion is filtered and the arsenic determined by the Gutzeit method.

At the 1919 meeting of this association the Referee on Insecticides, Winter<sup>3</sup>, suggested that it may be unnecessary to use carbon-dioxide-free water in determining water-soluble arsenic in lead arsenate, but the association took no action.

#### ZINC ARSENITE.

In 1917 Scott<sup>2</sup> published the following method for the determination of water-soluble arsenic in zinc arsenite:

A 1 gram sample is rubbed into an emulsion with several portions of water until the whole is in suspension. The cloudy liquor is diluted to 1,000 cc. and a portion filtered through a  $\frac{1}{4}$  in. asbestos mat on a perforated plate, the asbestos being covered with a layer of filter paper. The first 50 cc. are rejected. One hundred cc. of the clear filtrate (equals 0.1 gram) is treated with 10 cc. of strong sulfuric acid, 0.05 gram  $\text{Fe}_2\text{O}_3$  (use ferric ammonium sulfate) and  $\frac{1}{2}$  cc. of 80 per cent stannous chloride solution and heated until colorless. Arsenic is now determined by the Gutzeit method, using the larger sized apparatus.

Winter<sup>3</sup>, in 1919, recommended that a study be made of methods for the determination of soluble arsenic in zinc arsenite and in 1920 closely agreeing results were obtained by cooperating analysts using the 24-hour extraction method. The referee, Graham, in 1920<sup>4</sup>, and again in 1921<sup>5</sup>, recommended that this method be adopted as official.

<sup>1</sup> *J. Ind. Eng. Chem.*, 1917, 9: 682.

<sup>2</sup> Scott, Wilfred W. *Standard Methods of Chemical Analysis*, 1917, 32.

<sup>3</sup> *J. Assoc. Official Agr. Chemists*, 1921, 4: 395.

<sup>4</sup> *Ibid.*, 5: 50.

<sup>5</sup> *Ibid.*, 1922, 5: 403.

## EXPERIMENTAL.

In manufacturing arsenical insecticides it is necessary to secure the results of the chemical analysis of the product in the shortest time possible, so that if the material tests below standard a correction may be made. It is not practicable to wait 24 hours for the results for water-soluble arsenic as required by the present official method.

The following method has been in use a number of years in the control laboratory of one of the large insecticide manufacturers and has been found to yield results that agree closely with those obtained by the 24-hour method of this association. The method is applicable to lead arsenate and zinc arsenite, but not to calcium arsenate. Its applicability to Paris Green, London purple, and other arsenical insecticides has not been determined.

*Method.*

Add 2 grams of dry (or 4 grams of paste) lead arsenate or 1 gram of zinc arsenite to 100 cc. of cold water in a 400 cc. beaker, heat to boiling, and continue the boiling 5 minutes. Transfer to a 1 liter volumetric flask, make to volume, shake thoroughly, filter through a dry filter, transfer 250 cc. of the *clear* filtrate to an Erlenmeyer flask, add 3 cc. of concentrated sulfuric acid, and evaporate on a hot plate. When the volume reaches about 100 cc. add 1 gram of potassium iodide, and continue the boiling until the volume is about 40 cc. Cool, dilute to about 200 cc., and remove the excess iodine with 0.05N sodium thiosulfate, avoiding the use of starch solution at this point. Neutralize with sodium bicarbonate, add 4-5 grams in excess, and titrate with standard iodine solution to a permanent blue color, using starch solution as indicator. From the number of cc. of iodine solution used calculate the percentage of water-soluble arsenic in the sample.

Results on lead arsenate and zinc arsenite by this 5-minute boiling method and by the official 24-hour extraction method on a number of samples are shown in the table.

*Water-soluble arsenic (As) in lead arsenate and zinc arsenite as determined by different methods.*

SAMPLE No.	LEAD ARSENATE		ZINC ARSENITE	
	METHOD		METHOD	
	5-Minute	24-Hour	5-Minute	24-Hour
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	0.42	0.50	0.43	0.46
2	0.18	0.21	0.53	0.57
3	nil	0.04	0.49	0.55
4	0.06	0.10	0.32	0.35
5	0.21	0.16	0.24	0.28
6	nil	0.04	0.10	0.08

As shown by the above figures, the 5-minute method yields results agreeing very closely with those obtained by the association's 24-hour method.

## SUMMARY.

1. A review of previous work on methods for the determination of water-soluble arsenic in lead arsenate and zinc arsenite shows that this association has never tested methods requiring less than 5 hours for the extraction of the arsenic, and has not adopted any method requiring less than 24 hours for digestion.

2. Since a method that requires 24 hours or longer to get results is impracticable for the use of the insecticide manufacturer for manufacturing control, and uniform methods by both manufacturers and Federal and State inspection laboratories are highly desirable, it is suggested that this association seek to devise shorter methods for the determination of water-soluble arsenic in arsenical insecticides.

3. A method is presented that yields results closely comparable to those obtained by the present method of the association and that requires only 5 minutes for the extraction of the arsenic instead of 24 hours. It is applicable to lead arsenate and zinc arsenite but not to calcium arsenate.

## REPORT ON SOILS.

By W. H. MACINTIRE (Agricultural Experiment Station, Knoxville, Tenn.), *Referee*.

Other than the efforts of the Associate Referee for Sulfur in Soils and those of collaborators upon this subject, no work has been done upon methods for the analysis of soils. It had been anticipated that full revision would be called for through consideration by the Committee on Revision of Methods for Soil Analysis. Quite recently the referee has succeeded to the chairmanship of that committee and subsequent to correspondence and inquiries the committee is to meet for action on recommendations made prior to the 1923 meeting of the association.

## RECOMMENDATIONS.

It is recommended—

(1) That, subject to the action of the Committee on Editing Methods of Analysis, the methods for soils proposed by the Committee on Revision of Methods of Soil Analysis, be substituted for the existing tentative methods.

(2) That the report of the Committee to Cooperate with the American Society for Testing Materials on the Subject of Agricultural Lime be referred to Committee A, the Committee on Revision of Methods of Soil Analysis, and to the Committee on Editing Methods of Analysis, and, if approved, that the methods therein proposed be adopted as tentative methods for agricultural liming materials.

(3) That an associate referee be appointed to study methods and soil-to-water proportions for soil solutions in pH investigations.

## REPORT ON SULFUR IN SOILS.

By W. H. MACINTIRE (Agricultural Experiment Station, Knoxville, Tenn.), *Associate Referee*.

At the 1922 meeting of the association the Associate Referee on Sulfur in Soils recommended a further study of the problem. Additional work upon the nitric acid digestion procedure demonstrated that full recovery of total sulfur could not be assured. Though the method at first seemed simple and feasible, four possible vitiating factors appeared as unsurmountable barriers to its use. A study of an oxidative and fusion method was then undertaken by W. M. Shaw in the laboratory of the associate referee. Following preliminary work upon pure quartz, in order to determine empirically the optimum proportions of oxidative and fusion solids, the method was tried out on soils, with and without sulfate fortification. In these trials both soluble sulfates and barium sulfate precipitates were added to the soil. As a result of these studies the method offered by Shaw and MacIntire was evolved.

The directions and notes sent out to collaborators follow. Each collaborator was asked to subject the method to a critical comparison with the method that he considered the most accurate.

### PROCEDURE.

#### PREPARATION OF MIXTURE.

Place a 5-10 gram charge of 0.5 mm. fineness into a 100 cc. nickel crucible, add an equal weight of C. P. anhydrous sodium carbonate, and mix well with a stout nickel stirring rod of such length as to permit introduction into the furnace to be used in the fusion. Pipet carefully 4 cc. of water into each 10 grams of soil and stir well to a stiff paste, adding more water if necessary, a few drops at a time. Immediately add successive portions of about 1 gram of sulfur-free sodium peroxide, stirring well after each addition to obviate excessive frothing and overflow. Continue to add peroxide until the mixture becomes dry and granular and then add, as a surface coating, enough to make the total peroxide addition 25 grams per each 10 grams of soil. Place the mixture in an electric furnace.

#### FUSION OF MIXTURE.

Maintain a temperature of between 400° and 500° C. during the first half hour, raise the temperature rapidly to bright red heat (about 900° C.), and continue the fusion at this temperature for about 10 minutes. Withdraw the crucible from the muffle quickly, manipulate so as to cause the melt to spread out in a thin sheet over the interior of the crucible, and cool rapidly by contact with some good conductor in cool atmosphere.

#### DISINTEGRATION OF MELT.

Place the chilled crucible sideways in a 600 cc. beaker and immerse in distilled water. Add about 5 cc. of ethyl alcohol to decompose the sodium manganate. Cover the beaker with a watch glass, place on a cold electric hot plate, and apply heat. Boil briskly until all the melt is disintegrated (30 minutes is ordinarily sufficient). When the sus-

pension has assumed a flesh-colored, flocculent appearance, with no glassy green lumps of the melt in the interior of the crucible, remove the crucible and rod from the beaker and wash any flaky particles back into the beaker with the aid of a policeman, rinsing several times with hot water. (Should small glassy particles still cling to the inside of the crucible, disintegrate by boiling water in the crucible over the hot plate or a small flame and add the crucible content to the main volume.) Filter immediately by suction through a 9 cm. Büchner—a liter beaker placed under a bell jar being the most convenient arrangement.

#### FILTRATION AND WASHING.

When no more of the liquid can be drawn through the filter, return the residue, together with the filter paper, to the original beaker, washing any adhering particles carefully from the funnel. Add about 1 gram of sodium carbonate, macerate with the stirring rod, add 75 to 100 cc. of water, and bring to a brisk boil while stirring vigorously. Again throw onto a Büchner filter, suck nearly dry, and wash three or four times with about 20 cc. of hot water, to a volume of 500 cc. or 700 cc. for the 5 and 10 gram charges, respectively.

#### ACIDULATION OF FILTRATE AND DEHYDRATION OF SILICA.

Cover the beaker containing the filtrate with a watch glass and (important) place a supported funnel with its stem bent so it just reaches into the lip of the beaker. Through the funnel pour gradually about 80 cc. of concentrated hydrochloric acid per each 10 gram charge of soil, taking care that the acid runs down the side of the beaker. Slightly lift the cover glass and gently stir with a stirring rod, watching for strong effervescence. If effervescence does not ensue, add more acid immediately until it does. If the filtrate remains clear when concentrated to a volume of 400 cc., the barium sulfate precipitation may be effected immediately by the addition of barium chloride solution, with the silica remaining in solution.

However, to cover all cases, proceed as follows: Transfer acidulated filtrate to a shallow porcelain evaporating dish of 1000 cc. capacity as soon as effervescence has ceased. Place the dish 1 to 2 inches above an electric hot plate at full heat. When crystallization begins, raise the dish about 3 inches from the hot plate. Permit evaporation and dehydrate without stirring, breaking the surface crust occasionally to expedite evaporation.

#### PRECIPITATION OF BARIUM SULFATE.

To the dehydrated mass add 0.5 cc. of hydrochloric acid and 200 cc. of water. Dissolve the salts completely by warming. Filter off the silica on a Hirsch funnel using No. 2 Whatman filter, or paper of equivalent texture. Wash six times with hot water to a volume of about 400 cc. Heat the filtrate, add slowly 10 cc. of 5% barium chloride solution, and allow to stand overnight. Filter barium sulfate on a Gooch asbestos filter, ignite in an electric furnace (or place Gooch in a porcelain crucible over a burner flame), cool, and weigh.

#### NOTES AND SUGGESTIONS.

*Fusion mixture.*—Sodium carbonate serves both to moderate the speed of the oxidative process and to eliminate barium as barium carbonate in the first extraction. Optimum proportions of charge and sodium carbonate have been determined empirically by means of charges of pure quartz. The addition of sodium peroxide should be so regulated as to permit the comfortable handling of the crucible with the fingers, which will obviate excessive frothing and loss from overflow. Time is conserved by the



simultaneous mixing of a number of charges. Should solidification of the mixture occur at any time during the mixing process, it may be reverted to the pasty consistency by immersion of the crucible into hot water for a few minutes.

*Fusion of mixture.*—Speed is insured by the use of a large electric furnace, but any sulfur-free heat may be utilized. It is important that the specified temperature be not exceeded until the preliminary oxidation process has been insured, after which complete disintegration should be effected at a higher temperature. The formation of a thin layer of the melt and its rapid crystallization on the interior of the crucible are essential to maximum efficiency.

*Disintegration of melt.*—The melt is usually completely disintegrated by the procedure outlined. Aqueous digestion overnight offers no advantage. Furthermore, the successful use of the hot plate is conditioned upon the fact that the disintegration is started with a clear liquid in the beaker and with all the melt contained in the crucible. The presence of suspended material in the beaker at the beginning will make the use of the hot plate impossible on account of severe bumping, and a steam bath or water bath will have to be employed with a consequent delay of 2 or 3 hours in the process. The disintegration is completed by the action of the boiling water alone without any other mechanical agitation.

*Filtration and washing.*—The filtration of the alkaline aqueous extract removes iron, manganese, a good portion of the aluminium, all the barium, and earthy bases—mostly in the form of carbonates and silicates.

*Acidulation of filtrate and dehydration of silica.*—The covering of the beaker and addition of acid as directed, rather than pouring in and stirring with a rod, is most important. Often no silica precipitation takes place, particularly if the solution is left to come to room temperature prior to addition of acid, even after subsequent concentration to a volume far below that from which the barium sulfate precipitation is made. By this procedure the dehydration process is also greatly facilitated and expedited. The silica usually comes out as coarse crystals after some sodium chloride has crystallized, and the full evaporation and dehydration is accomplished in about 4 hours. The use of inverted tripods on the hot plate affords a very convenient means of adjusting the distances for the evaporation and dehydration of the silicic acid.

Barium chloride additions show no detrimental effect upon sulfate recoveries and sulfates added to the melt as barium sulfate are completely recovered.

#### COMMENTS BY COLLABORATORS.

*New Jersey Station.*—Using the proposed procedure parallel with the calcium nitrate method<sup>1</sup> with unfertilized soils H. C. McLean obtained the results given in Table 1.

<sup>1</sup> *Texas Expt. Station Bull.* 302, 9.

TABLE 1.

*Total sulfur in soils.*

(Corrected results reported as grams of barium sulfate obtained from 10 gram soil.)

SOIL NO. 1			SOIL NO. 2	
DETERMINATION NO.	PEROXIDE FUSION	CALCIUM NITRATE FUSION	PEROXIDE FUSION	CALCIUM NITRATE FUSION
1	0.0430	0.0298	0.0280	0.0212
2	0.0408	0.0284	0.0274	0.0209
3	0.0410	0.0301	0.0280	0.0212
4	0.0400	0.0295	0.0269	0.0229
Average....	0.0412	0.0295	0.0276	0.0216

McLean commented as follows: "It will be noted that the peroxide method gave the highest amount of sulfur in each case. Although this method is very long and tedious, it appears to give better results than any so far worked out, and should no doubt be recommended as being the most desirable for the determination of sulfur in soils".

*Oregon Station.*—The results obtained by D. E. Bullis of the Oregon Station on two fortified and unfortified soils are given in Table 2.

TABLE 2.

*Total sulfur in soils, 5 gram charge.*

(Results corrected for blank on reagents.)

## BARIUM SULFATE

SAMPLE	OLD METHOD*			PROPOSED METHOD		
	Added	Weighed	Recovered	Added	Weighed	Recovered
	<i>gram</i>	<i>gram</i>	<i>gram</i>	<i>gram</i>	<i>gram</i>	<i>gram</i>
Willamette Clay Loam..	.. . . .	0.0137 0.0136 0.0109	.....	.....	0.0149 0.0140	.....
Willamette Clay Loam..	0.0500	0.0527 0.0505 0.0658 0.0653	0.0400 0.0378 0.0531 0.0526	0.0500	0.0559 0.0573	0.0414 0.0428
Sites Silty Clay Loam...	.....	0.0081 0.0126	. . . . .	.....	0.0107 0.0090	.....
Sites Silty Clay Loam...	0.0500	0.0480 0.0474	0.0376 0.0370	0.0500	0.0506 0.0517	0.0408 0.0419

\*"Old Method" is the ordinary sodium peroxide fusion, removing silica, precipitating sulfur as barium sulfate, filtering, and igniting after 48 hours on asbestos Gooch filters.

In transmitting the results J. S. Jones stated: "We are far from satisfied with the old method and are certainly very much interested in any method that promises more uniformly concordant results. You will note, however, that in following the proposed new method we did not recover all of the *barium sulfate* added. In this we are dis-

appointed in view of the statement that you made with reference to your success in recovering added sulfur \* \* \*. Our Mr. Bullis is of the opinion, however, that the procedure as a whole is a decided improvement over the old ones". It will be noted that Bullis recovered over 80 per cent of a heavy addition of barium sulfate, one per cent, an amount many times in excess of the expectancy for barium occurrences in soils.

*Tennessee Station.*—The work done at this station has been reported by Shaw and MacIntire<sup>1</sup>. These results demonstrated the fallacy of the use of hydrochloric acid in making solutions of soil melts. They also pointed out many advantageous features, such as the use of larger charges, elimination of alkali earths and iron, and in most cases lack of necessity for elimination of silica, together with the recovery of any such insoluble sulfur occurrences as barium sulfate. Complete disintegration and a perfect melt at relatively low temperature were secured. The melt was found to undergo ready disruption and partial solution. The minimum of undesirable potassium salts, during the barium sulfate precipitation, is also insured.

#### RECOMMENDATION.

As a result of the three years' work on a method for the determination of sulfur in soils, it is recommended that the sodium-peroxide-sodium-carbonate method, as given in this report, be referred to the Committee on Revision of Methods for Soil Analysis and be included in the revised methods in case of favorable action by that committee.

No report on the determination of active acidity, or hydrogen ion concentration, for agricultural products was made by the associate referee.

#### REPORT ON FOODS AND FEEDING STUFFS.

By L. E. BOPST (State Control Department, College Park, Md.),  
*Referee.*

The Committee on Recommendations of Referees recommended that the Referee on Foods and Feeding Stuffs study further methods for the determination of ether extract in various foods and feeding stuffs to ascertain whether or not the official method<sup>2</sup> is applicable to all the products for which it is now being used. The referee last year, J. B. Reed, reported that the C. R. Smith method<sup>3</sup> gave practically the same results as the official method for ether extract in wheat by-products and recommended a further study on mixed feeds.

To comply with this recommendation various feeds were selected representative of the more common ones found in intrastate commerce, and crude fat was determined upon each by the official method and by the C. R. Smith method. The average results obtained by the two methods are shown in Table 1.

<sup>1</sup> *J. Ind. Eng. Chem.*, 1923, 15: 1183.

<sup>2</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 72.

<sup>3</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 61.

TABLE 1.

*Ether extract determinations by two methods.*

	OFFICIAL METHOD	C. R. SMITH METHOD
	<i>per cent</i>	<i>per cent</i>
Alfalfa Meal.....	1.80	2.08
Cottonseed Meal.....	7.13	9.02
Linseed Meal.....	8.03	7.90
Corn and Oat Chop....	3.97	3.85
Wheat Bran.....	5.68	5.50

The results show very little difference in the actual fat content obtained by the two methods, with the exception of cottonseed meal. They indicate that the use of the more complicated and especially expensive C. R. Smith method is not warranted in making ether extract determinations on wheat by-products and mixed feeds, since the official method gives practically the same results.

The committee also recommended that further study be made of the effect which grinding the sample finer will have upon the ether extract determinations. Following this recommendation, different types of samples were treated by the official method, the Knorr apparatus being used, and the results given in Table 2 were obtained.

TABLE 2.

*Ether extract determinations on samples of different degrees of fineness.*

	20-MESH	40-MESH	60-MESH
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Bran .....	5.68	5.85	5.83
Alfalfa Meal .....	1.80	1.84	1.84
Cottonseed Meal.....	7.13	7.16	7.24
Linseed Meal.....	8.03	8.14	8.27
Corn and Oat Chop....	3.97	3.98	4.12

It would seem that the finer the sample is ground, to the point where it is impracticable to grind it further, the more ether extract is obtained. However, granting that this is true, the procedure is to a large extent impracticable. Wheat bran, oats, cottonseed meal, and other substances of a similar nature are very difficult to grind even through a 20-mesh sieve. If an attempt is made to get them finer, a great amount of time and work is involved, especially in State control laboratories where thousands of samples have to be ground and the results published at stated intervals, and where the element of time is an important factor.

The collaborative work in this investigation was done by A. L. Flenner, of the Maryland State Control Laboratory.

It occurred to the referee that a cellulose solvent might be used to break down the cell walls and membranes, and thereby liberate more material that could be extracted by the ether. For a trial, 3 grams

of bran finely ground were treated with 40 cc. of zinc chloride for three hours at 75° C. Only a small amount of the bran went into solution, which became extremely colloidal in nature. It was practically impossible to filter. The extract, dried in a continuous extractor, gave a black sirupy residue that weighed 0.74 grams. Cupric ammonium hydroxide was next tried, and a residue of the same colloidal nature, which could not be filtered, was obtained. It was diluted with water, and a small amount of salt was added. Apparently this broke up the colloidal state for filtration was then possible.

This work, in general, was not productive of results that would lead to any improvement or change in the present official method for fat. It was found by Smith, working in the Baltimore Station of the Bureau of Chemistry, (1) that digestion with 1.25 per cent sulfuric acid removed about 20 per cent of the total ether extract; (2) that the subsequent 1.25 per cent alkali solution and washing with water removed about 65 per cent of the total ether extract; and (3) that about 15 per cent of the total ether extract remains after both digestions and washings. This work was verified by the referee. No treatment of feeds with sulfuric acid prior to extraction with ether will increase the results in any way.

The committee recommended also that the referee study the existing official methods for water in foods and feeding stuffs. It is regretted that the apparatus ordered for this work was not received in time to comply.

#### RECOMMENDATIONS.

It is recommended—

(1) That the work on the comparison of the official method and the C. R. Smith method for ether extract determinations be dropped, (1) because the differentiations in the results in mixed feeds and in wheat by-products are not sufficient to warrant the use of the C. R. Smith method; and (2) because the C. R. Smith method is more complicated and expensive.

(2) That further study of the effect which grinding the sample finer will have upon the ether extract determinations be dropped. While the results show conclusively that the finer a sample is ground the more fat may be extracted, this procedure is considered impractical in grinding all types of feed.

(3) That the referee be requested to study the existing official methods for the determination of water in foods and feeding stuffs, with a view to rewording and fixing rigidly the conditions of temperature, pressure, and other factors.

(4) That a definite method for the determination of water in dried food be formulated and submitted to the association.

## REPORT ON CRUDE FIBER.

By H. H. HANSON (State Board of Agriculture, Dover, Del.), *Associate Referee*.

In the beginning some one coined the term "crude fiber", and it has been under discussion ever since.

Your associate referee for this year, upon receipt of notification of his appointment last December, immediately began a preliminary survey of the situation through the printed proceedings of this association, by correspondence with several preceding referees and members long experienced in this line of work, and by personal conferences with several members including the General Referee on Feeding Stuff, members of the Bureau of Chemistry, and others.

When the writer first became a member of the A. O. A. C., about twenty years ago, crude fiber was a regular subject of study, and it is related that the matter has been under discussion since the birth of the association. Some ten years ago it began to receive particular attention, and a special effort was made to revise the official method. About that time, C. K. Francis of Oklahoma made an important study of this subject.

## PROGRESS TOWARD IMPROVING METHOD.

No definite progress seems to have been made, however, until 1920, when G. L. Bidwell presented an exhaustive paper by Bidwell and Bopst, showing the varying results obtained by certain different manipulations and procedures. Nine different points involved in the process were studied thoroughly and discussed, and a new method for crude fiber was suggested.

In 1921, a revision of this method was proposed for adoption by this association, and it was the recommendation of Committee B that the official method be deleted and the one proposed by the referee be substituted. Last year, G. S. Fraps, referee, after a careful study of the method and of the results obtained by a large number of collaborators, offered the following recommendation, which was adopted: "That the referee consider the criticisms made of the proposed new method by the collaborators this year and make such study as may be necessary in order to make a final report relative to the substitution of the proposed method for the official method".

The method for the determination of crude fiber has been changed in minor details in so many of the official laboratories that it is difficult to find two analysts that are making crude fiber determinations in exactly the same manner. The variations are, for the most part, slight, but Bidwell and Bopst showed conclusively that some of them had an important influence on the results obtained. Their new method has

occasioned much study and some criticism upon certain points. It seemed to the associate referee this year that after all these years of experience and investigations enough collaborative work had been done and enough data were at hand for the association definitely to decide upon an official method that could be adopted by all laboratories and that would give reasonably concordant results in the hands of different workers.

In order to obtain the opinions of numerous feed chemists, the referee sent letters to thirty-seven different workers interested in crude fiber, requesting their opinion upon four points of the method in particular and any other discussion of the method that they saw fit to make. The points upon which particular discussion and information was requested were the fineness of the sample, the condenser to be used, the use of asbestos, and the manner of making the second filtration. Twenty-nine replies were received, which, it should be remembered, embodied the ideas of different analysts of feeding stuffs throughout the country, most of them many years in the work.

#### FINENESS OF MATERIAL.

The associate referee suggested that for the determination of crude fiber samples should be uniformly ground to pass a 40-mesh sieve. All the answers agree that the fineness of the sample should be specified, and that it should be uniform. Several call attention to the fact that as the general methods for foods and feeding stuffs already prescribe the fineness of the sample, a different degree of fineness for this particular method would not be desirable. Seven are in favor of grinding to pass a 40-mesh sieve, while thirteen are of the opinion that this is too fine and that a 20-mesh sieve would be preferable.

After reviewing the replies received and taking into consideration the fact that it is difficult, if not impossible, to grind certain classes of feed to pass a 40-mesh sieve, the conclusion has been reached that the sample used for crude fiber should be ground as specified under Foods and Feeding Stuff<sup>1</sup>, which is practically equivalent to grinding to pass a 20-mesh sieve.

#### CONDENSER.

The associate referee called attention to the fact that the condenser is used solely for the purpose of preventing a loss in the solutions and suggested that the analysts be allowed any efficient condenser—that is, any condenser that will absolutely preserve the volume of the solution throughout the operation. In the answers received, three express no opinion; three others are of the opinion that the condenser used should be specified and that all condensers should be alike; two are certain that

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<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 71.

the water-jacketed condenser, such as was recommended by Bidwell and Bopst, should be used; while twenty agree that any efficient condenser should be allowed.

No doubt a water-jacketed condenser about 15 inches long, as specified, will preserve the volume of the solution as efficiently as any condenser that it is possible to use. However, a battery of such condensers is expensive and easily broken, and the connections must be continually renewed. As several other types of condensers in use in different laboratories are also efficient and prevent absolutely any diminution in the volume of the liquid, there does not seem to be any good reason why they should not be allowed. For example: In one laboratory in which the writer worked for some years, the condenser consisted of a large metal tank of water through which extended a series of block tin tubes, similar to the ordinary nitrogen distillation apparatus. The effect of this condenser was exactly that of the one suggested in the Bidwell-Bopst method. The writer is now using as condensers air-cooled glass tubes that are attached to Erlenmeyer flasks by means of rubber stoppers, and as these tubes are 100 cm. long and 10 mm. inside diameter they prevent absolutely any loss in volume. The conclusion upon this point, therefore, is that any absolutely efficient condenser may be used.

#### USE OF ASBESTOS.

On the question of the use of asbestos one analyst expresses no opinion; one would use no asbestos or exempt certain materials; three agree that the method should be specific but express no preference; one, no asbestos or optional; five, no asbestos; four, asbestos with all samples; four, limit the use of asbestos to feeds having a certain per cent of fiber; and nine, exempt certain products but use asbestos with others.

It is upon this point that the greatest divergence of opinion exists. Bidwell and Bopst have shown in a previous report<sup>1</sup>, and their conclusion is corroborated by other analysts, that the use of a small amount of asbestos during the process facilitates filtration with some classes of feeds. The complaint has been made by many analysts that the use of asbestos increases the bulk of the sample to such an extent that it is difficult to handle, especially during the last filtration. The use of asbestos with certain kinds of feeding stuffs, as far as importance in filtering is concerned, is negligible; for example, with ground alfalfa, hays, corn silage, and such bulky fodders and feeds. Bidwell and Bopst have shown also that the use of asbestos with certain materials does influence the final result. After a thorough study of the subject, the use of asbestos with certain classes of feeds seems highly desirable, while with others the asbestos itself answers no purpose, and if it were

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1921, 5: 58.



possible to outline a method by which all analysts could be governed at all times, making the use of asbestos obligatory at certain times and leaving it out at others, such a course would seem to be the most logical, if it were not for the fact that in many laboratories at the present time the fiber determination is made upon the same charge that has been used for the fat extraction. and that during this process asbestos is already introduced into the charge. To eliminate asbestos arbitrarily, therefore, with a certain class of feeds would mean that the method for the determination of fat would have to be changed also, and this does not seem at all desirable. Therefore, taking into consideration the fact that many laboratories use asbestos in their fat determinations and also the fact that the use of asbestos is desirable with certain classes of feeds, it has been deemed wise to incorporate its use in the suggested method but to restrict the amount to about one-half gram.

#### SECOND FILTRATION.

The opinions on a second filtration may be summarized as follows: One analyst makes no remarks; one suggests that the second filtration should be optional; five prefer the use of alundum crucibles; eight prefer filtering directly into Gooch crucibles with asbestos; and thirteen prefer to use linen for the second filtration and then transfer to the Gooch crucible for drying and weighing.

It will be seen from these answers that no method can be suggested that will agree entirely with the personal preferences of the different analysts who make up this association, but it is hoped that the method to be recommended in this report can be adopted by the association and by all the laboratories of the country, in order that the official work on crude fiber may be uniform.

As was pointed out by Bidwell and Bopst, the determination of crude fiber is not the determination of a definite chemical substance. They call the method a "definitive" one, a method in which the process itself defines the result. Concerning this point, G. S. Fraps wrote last year as follows: "If this method is a definitive one, there is no more reason for taking the method of boiling in a flask with a Liebig condenser as the standard than for taking the method of boiling in a beaker with a round condenser. One method might give slightly different results, but either method could be adopted as a standard. If more uniform results could be secured by one, or by the other method, it should be given the preference".

According to the method as proposed by Bidwell and Bopst, the second filtration takes place directly into a Gooch crucible. It seems to be the consensus of opinion of those who answered the questions of the associate referee that the second filtration should be made upon linen, and that after washing the charge should be transferred to the Gooch

crucible. It has been the experience of many analysts, including the writer, that unless the alkali is washed from the charge before transferring to the Gooch crucible, this filtration in many instances is a very slow process. It is also the opinion expressed by many that it is much easier to transfer the charge from the boiling flask to the linen filter than to transfer it from the boiling flask to the Gooch crucible. After thorough washing on the linen, there is no difficulty in making the transfer and usually there is no time saved by attempting to make the filtration directly into the Gooch. However, eight correspondents prefer to filter directly into the Gooch, and this procedure has been shown to be perfectly feasible.

The growing popularity of the alundum crucible for use at this point has been marked, and if it is preferred for the second filtration there would seem to be no reason why it should be prohibited.

Taking up again in their order the four points particularly discussed in this paper, namely, fineness, condenser, asbestos, and second filtration, and after considering the replies received and the importance of making recommendations that can be followed not only without difficulty but with a view to uniformity of results, the writer has arrived at certain conclusions, which have been incorporated in the proposed new method. It should be understood that the conclusions finally drawn have not in all cases been in accord with the previous practice of your associate referee, but an attempt has been made not to allow personal prejudices to influence the changes outlined in the method.

The method as rewritten is as follows:

#### REAGENTS.

(a) *Sulfuric acid solution*.—Contains 1.25 grams of sulfuric acid per 100 cc.

(b) *Sodium hydroxide solution*.—Contains 1.25 grams of sodium hydroxide per 100 cc., free, or nearly so, from sodium carbonate.

(The strength of these solutions must be accurately checked by titration.)

(c) *Asbestos*.—First digest on the steam bath overnight with 5-10% of sodium hydroxide and thoroughly wash with hot water; then digest overnight with 5-10% of hydrochloric acid and again wash thoroughly with hot water; and finally ignite completely at bright red heat.

#### APPARATUS.

##### *Condenser.*

Any condenser may be used that will absolutely preserve the volume of the solutions throughout the entire process of digestion.

##### *Container.*

The form of the container should be such that the depth of the solution will not be less than one inch or more than one and one-half inches and should permit the attachment of the condenser and rotation of the container. A 700-750 cc. Erlenmeyer flask is recommended.

*Filtering Cloth.*

The filtering cloth should be of such character that while filtering is rapid no appreciable amount of solid matter passes through. Either butcher's linen or dress linen with about 45 threads to the inch, or No. 40 filtering cloth made by the National Filter Cloth and Weaving Company, 57 Hope Street, Brooklyn, New York, may be used.

## DETERMINATION.

Extract 2 grams of the dry material with ordinary ether, or use the residue from the ether extract determination and transfer the residue, together with about one-half gram of asbestos, to the container. (Where the residue from the ether extract is used, and the proper amount of asbestos has already been added, further addition is unnecessary.) Using a calibrated beaker, add 200 cc. of boiling sulfuric acid (a) to the contents of the flask, place immediately on a heating battery, and connect with the condenser. Bring the contents of the flask to boiling within one minute after placing on the battery and continue boiling briskly for exactly thirty minutes. Rotate the flask about every 5 minutes in order to mix the charge thoroughly. Use care to keep the sides of the flask above the solution free from the sample. (A blast of air conducted into the flask will serve to reduce the frothing of the liquid.) Remove the flask at the expiration of the 30 minutes, immediately filter through linen in a fluted funnel, and wash with boiling water until the washings are no longer acid.

Wash the charge and adhering asbestos back into the flask with 200 cc. of boiling sodium hydroxide solution (b), using a calibrated 200 cc. wash bottle. Bring the sodium hydroxide to boiling and keep at this temperature under a reflux condenser while in use. (The sodium hydroxide is transferred most easily to the 200 cc. wash bottle by means of a bent tube through which the liquid is forced by blowing into a tube connected with the top of the condenser.) Place the flask in the heating battery, connect with the reflux condenser, and boil for exactly 30 minutes. Time the boiling with the alkali so that the contents of the different flasks will reach the boiling point approximately 3 minutes apart, and thereby provide sufficient time for filtration. Remove the flask at the expiration of the 30 minutes and immediately filter through the filtering cloth into a fluted funnel, into an alundum crucible, or directly into the Gooch. If cloth is used, wash the charge thoroughly with boiling water before transferring it to a Gooch crucible, previously prepared with a thin but close layer of ignited asbestos, and then wash with about 15 cc. of 95% alcohol.

Dry the crucible with its contents to constant weight at 110° in an electric oven, usually overnight. After weighing, incinerate the contents of the crucible in an electric muffle or over a Meker burner at a dull red heat until the carbonaceous matter has been removed (20 minutes is usually sufficient). Cool in an efficient desiccator and weigh.

The loss in weight is taken as crude fiber.

## RECOMMENDATIONS.

It is recommended—

(1) That the method for the determination of crude fiber as given in this report be adopted as official.

(2) That the modification proposed for prepared mustard or similar pasty material, as published<sup>1</sup>, be incorporated under the head of Spices.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 6: 344.

## REPORT ON METHOD FOR THE DETERMINATION OF STARCH IN THE PRESENCE OF INTERFERING POLYSACCHARIDES.

By MAYNE R. COE (Bureau of Chemistry, Washington, D. C.),  
*Associate Referee on Starch.*

All work on the method for the estimation of starch in the presence of interfering polysaccharides has been directed this year toward the value of the method as a means of detecting adulteration of linseed meal. As the original paper<sup>1</sup> states, pure linseed meal contains no starch, and while commercially cleaned linseed contains a small amount of starch a large amount would show adulteration.

Samples of linseed meal containing 3.28 per cent only of foreign material and samples of the same meal containing added starch were sent out to collaborators. The following results were received:

	Linseed Meal			Linseed Meal and Starch			
	Average of all—1.41 %.			Theoretical—5.83 %.			
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
C. E. Goodrich Hyattsville, Md.	.	1.19	1.34	...	5.06	5.38	5.20
M. Jongeward, Fargo, N. D.	. .	..	. .	5.59	5.51	5.56	6.29
H. E. Gensler, Harrisburg, Pa.	2.24	2.52	2.38	. .	3.99	4.38	4.19
L. C. Mitchell, Minneapolis, Minn.	0.61	0.50	1.01	. .	4.44	4.97	2.39
M. R. Coe	. .	1.08	1.23	...	6.08	5.69	6.51

It will be noted that the results for meal with added starch vary somewhat, but taken as a whole they are good. since the difficulty of preparing a uniform sample with a definite amount of starch is well known. The results on straight linseed cake by three of the four collaborators agree reasonably well with those obtained by the associate referee, who is most familiar with the procedure. It is realized that the method is unusually involved and requires some experience to obtain results that are dependable. However, the wide variation as a whole may be due to incomplete precipitation of the interfering polysaccharides.

A change of procedure is recommended at the point of gelatinization. Instead of using a 300 cc. Florence flask, transfer the sample directly to a 500 cc. volumetric flask and add not more than 25 cc. of cold water

<sup>1</sup> Walton, G. P. and Coe, M. R. Determination of starch content in the presence of interfering polysaccharides. *J. Agr. Research*, 1923, 23: 995.

to wet the sample thoroughly. Shake violently and allow to stand 10 minutes or more. When the boiling water is added again shake vigorously, and thus obtain a solution free from lumps.

#### RECOMMENDATION.

It is recommended that further study of this method be made, and that attention be given to a more complete precipitation of the interfering polysaccharides before a recommendation for adoption as official is made.

### REPORT ON STOCK FEED ADULTERATION.

By H. E. GENSLER (State Department of Agriculture, Harrisburg, Pa.),  
*Associate Referee.*

During the year the Referee on Stock Feed Adulteration submitted samples of material for examination and methods of procedure to fifteen collaborators. Of this number, seven made determinations, and their results are included in the accompanying tables.

Because of the excellent results obtained by collaborators in the determination of rice hulls in rice bran, it was suggested that a similar method might be used to determine oat hulls in oats, in order to ascertain whether or not hulls had been added. Samples were prepared, therefore, consisting of oats and oat hulls. Sample 1 consisted of oats ground to pass through a 40-mesh sieve. Samples 2, 3, 4, 5, and 6 were made by adulterating Sample 1 with various amounts of oat hulls to the extent of 10, 5, 15, 8, and 5 per cent of hulls, respectively. Samples 1, 2, 3, and 4 were "known" samples to be used in making standard counts; Samples 5 and 6 were the "unknowns", upon which determinations were to be reported.

The collaborators were instructed to make microscopic counts of the number of hull particles found in a 4 milligram portion, after treatment with sodium hydroxide solution (1.25%), using a slide ruled in parallel lines one-twentieth of an inch apart. Special attention was called to the fact that only particles that showed one or more cross striations, due to fracture, should be included in the count. This point of technique was advised by the referee, because he was able to obtain consistent results in making this determination only when all other tissues of the hull were disregarded.

A study of the results obtained by the collaborators, given in Table 1, shows a wide variation in the number of particles counted, as well as in the percentage of hulls found. All the collaborators obtained counts on the "standards" proportionate to the amount of hulls present. Their reports on the "unknowns" also showed adulteration in every

case, although the percentages of added hulls obtained were not always consistent with the amounts actually present. Collaborators 5, 6, and 7 obtained results very close to the correct figures.

TABLE 1.  
*Determination of oat hulls in oats.*

ANALYST	AVERAGE COUNTS ON STANDARDS				COUNTS ON UNKNOWNNS			
	Sample 1, Oats	Sample 3, 5% Hulls	Sample 2, 10% Hulls	Sample 4, 15% Hulls	Sample 5, 8% Hulls		Sample 6, 5% Hulls	
					Average Count	Per Cent	Average Count	Per Cent
1	114	131	149	167	161	13.5	124	2.8
2	46	51	56	70	66	12.5	57	11.0
3	205	247	285	331	313	13.0	256	6.0
4	270	295	329	373	386	16.0	398	17-18
5	.	.	.	.	.	10.0	..	5.6
6	.	.	.	.	.	App. 7.0	..	App. 5.0
7	.	.	.	.	.	10.0	..	5.0

From the results obtained, it appears that it is possible to ascertain whether or not samples of oats contain excessive amounts of hulls, although the individual analyst must be guided by his own experience and ability to determine the amount or percentage of hulls present in "known" samples. Different lots or grades of oats vary in the proportion of hulls that they contain, and continued work along this line would be necessary before the method could be adopted.

TABLE 2.  
*Determination of salt in feeding stuffs.*

ANALYST	SAMPLE 7, 1/2% SALT	SAMPLE 8, NO SALT
1	Present	Bare trace
2	Present	None present
3	Present	None present
4	Present	Present
5	Present	None present
6	Present	Present
7	Present	No salt

Samples 7 and 8 were submitted to the collaborators to try out a method devised by the referee for detecting free salt in feeding stuffs. Salt is often claimed as an ingredient, and the microanalyst must determine whether or not it is present. Inasmuch as chlorides are also present as a natural component of the ingredients of feeds, a chemical determination would give a positive test if made on a solution or ash prepared from the sample. The analyst could not, therefore, say with

certainty from such tests that salt was not present even though it might not have been added as one of the ingredients. For this reason the referee submitted the following method for detecting salt in stock feeds:

Transfer 2 cc. of a 5% solution of silver nitrate to a small test tube of 1 cm. internal diameter. Carefully add to this liquid an equal volume of the feed, which has previously been ground to pass a millimeter sieve, so that most of the sample floats or remains above the liquid. When the tube is gradually inclined the liquid is absorbed, and white patches of silver chloride appear wherever the minutest crystal of salt comes in contact with the solution. These patches may easily be observed with a lens or even with the naked eye.

Sample 7 was wheat middlings containing one-half of 1 per cent of salt; Sample 8 was a molasses feed, containing no added salt. Table 2 shows that accurate results were reported by all the analysts on Sample 7. Analysts 1, 4, and 6 reported the presence of salt in Sample 8. Inasmuch as this sample was a molasses feed, it is evident that their conclusions were based upon the slight turbidity that molasses is likely to give.

#### RECOMMENDATIONS.

It is recommended—

(1) That a further study be made of the method for the detection of free salt in feeding stuffs.

(2) That work along the lines already adopted for determining ingredients in stock feed be continued.

#### REPORT OF THE REFEREE ON SACCHARINE PRODUCTS.

By H. S. PAINE (Bureau of Chemistry, Washington, D. C.),  
*Referee.*

Three of the four associate referees on saccharine products have been active this year, those on sugar-house products, honey, and maltose products. Unfortunately, owing to delay in securing an Associate Referee on Maple Products, it has been impossible to accomplish much on this subject. It was considered fitting that the work on maple products be continued for a period under the direction of a Canadian chemist. H. M. Lancaster, recently appointed chief analyst of the Food and Drug Laboratory of the Canadian Department of Health, consented to act as associate referee. No formal report was received. The work contemplated consists particularly in passing definitely upon the Canadian lead number and the conductivity method developed by J. F. Snell of Macdonald College.

The referee concurs in the recommendation made by the Associate Referee on Honey that further investigation be made relative to the application of the resorcin and aniline chloride tests to honey that has

been stored for varying lengths of time after having been heated to temperatures that would prevail in the ordinary commercial handling of the product.

The referee also concurs in the recommendations made by the Associate Referee on Sugar-House Products and suggests that the program outlined for next year be followed. The work on sugar-house products included both cane and beet sugar products.

## REPORT ON HONEY—DETECTION OF ARTIFICIAL INVERT SUGAR IN HONEY<sup>1</sup>.

By SIDNEY F. SHERWOOD (Bureau of Plant Industry, Washington, D. C.), *Associate Referee*.

In the report on honey relative to methods for detecting artificial invert sugar, presented by the writer at the 1921 meeting, it was concluded that in the case of honeys that have been heated at temperatures that would prevail in the ordinary commercial handling of this product, neither the resorcin nor the aniline chloride test affords results that can be construed to indicate the presence of artificial invert sugar, and that a positive test, therefore, would seem to indicate the presence of a foreign substance. As the number of collaborators was small and certain variations in the tests were reported in 1921, it was recommended that the work be repeated and that the character of the color developed in the tests be described more fully than has been done in the Book of Methods<sup>2</sup>.

The work was continued in 1922, but insufficient data precluded a report at the annual meeting. The results obtained are included in this report.

The samples sent out in 1922 were the following:

No.	NAME	ACIDITY per cent
1	Tupelo.....	0.10
2	Clover .....	0.12
3	Clover*.....	0.37
4	Honeydew....	....

\*Contained added tartaric acid: 2 grams to 500 grams of honey.

The samples sent out in 1923 were the following:

No.	NAME	ACIDITY per cent
1	Buckwheat.....	0.11
2	Clover.....	0.09
3	Buckwheat and Clover*.....	0.30
4	Honeydew.....	0.13

\*Contained added tartaric acid: 2 grams to 500 grams of honey.

<sup>1</sup> Presented by W. Seaman.

<sup>2</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 112.



The acidity was determined as reported in 1921<sup>1</sup> and is expressed as per cent free acid as formic.

The samples were treated as follows:

Series A.—Heated for 1 hour at 160° F. (71.7° C.).

Series B.—Heated for ½ hour at 180° F. (82.2° C.).

Series C.—Heated for 20 minutes at 208–209° F. (97.8°–98.3° C.).

Series X.—Honey plus 20 per cent of commercial invert sugar sirup.

As the samples were not artificially cooled the actual time of heating was longer than that given.

Directions for making the tests were identical with those given in the report of 1921, but the color reaction indicating a positive test was described more explicitly than in the *Book of Methods*. The collaborators in 1922 were C. G. Church, Fruit and Vegetable Chemistry Laboratory, Bureau of Chemistry, Los Angeles, Calif., and C. P. Wilson, Exchange Research Laboratory, San Dimas, Calif. Those in 1923 were Church; Willard Baier, Exchange Research Laboratory, San Dimas Calif.; and M. S. Badollet, Carbohydrate Laboratory, Bureau of Chemistry, Washington, D. C.

The associate referee wishes to express his appreciation of the assistance given by the collaborators throughout the investigation.

The reports from the collaborators are given in Tables 1 and 2.

Bearing in mind the fact that a positive reaction consists of a cherry red color appearing at once and that yellow to salmon shades of color appearing upon standing do not indicate a positive test, examination of the results may be summarized as follows:

*Resorcin test (Bryan's modification of Fiehe's test).*—Each collaborator obtained a negative test in every sample in every series, though it should be noted that three of them obtained a negative test in the Sample X that contained 20 per cent of added commercial invert sugar sirup. These results are in agreement with the 1921 results even to the extent that several of the collaborators in 1921 obtained a negative test on the sample containing added commercial invert sugar sirup. While none of the 1921 collaborators reported "positive", in several cases they reported "doubtful" or "slight trace"; this was probably due to uncertainty as to the color indicating a positive reaction.

*Aniline chloride test (Feder's).*—Each collaborator obtained a negative test in every sample in every series with the exception of one report of "suspicious" in Sample 4, Series A, though one of them obtained a negative test in the Sample X containing 20 per cent of added commercial invert sugar sirup, and two of them obtained merely suspicious results on this sample. As in the case of the resorcin test, the results are in entire agreement with the 1921 results even to the extent that two of

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 429.

the 1921 collaborators reported negative in the case of the sample containing commercial invert sugar sirup. They also showed apparent uncertainty as to the color indicating a positive reaction.

Previous investigations covering a great number of samples of honey of practically every variety show conclusively that normal honey never affords a positive test with either the resorcin or the aniline chloride test. Summing up the result of three years' investigations on heated honey the same conclusion appears to be correct in the case of honeys

TABLE 1.  
*Resorcin Test.*  
(Bryan's modification of Fiehe's test.)

SERIES A.

1922					1923			
No	Time	Church	Wilson	Sherwood	Church	Baier	Badollet	Sherwood
1	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Negative	Negative	Negative	Negative	Negative
2	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Suspicious	Negative	Negative	Negative	Negative	Negative
3	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Suspicious	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Positive	Negative	Negative	Negative	Negative	Negative
4	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Suspicious	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Positive	Suspicious	Suspicious	Suspicious	Negative	Suspicious

SERIES B.

1	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Suspicious	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Positive	Negative	Negative	Negative	Negative	Negative
2	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Suspicious	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Positive	Negative	Negative	Negative	Negative	Negative
3	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Negative	Negative	Negative	Negative	Negative
4	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Suspicious	Negative	Suspicious	Suspicious	Negative	Suspicious

SERIES C.

1	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Negative	Negative	Negative	Negative	Negative
2	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Negative	Negative	Negative	Negative	Negative
3	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Suspicious	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Suspicious	Suspicious	Negative	Negative	Negative
4	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Suspicious	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Suspicious	Suspicious	Negative	Negative	Suspicious

SERIES X.

X	Immediate	Positive	Negative	Positive	Negative	Negative	Positive	Positive
	1 minute	Positive	Negative	Positive	Suspicious	Suspicious	Positive	Positive
	5 minutes	Positive	Negative	Positive	Positive	Suspicious	Positive	Positive

TABLE 2.  
Aniline Chloride Test.  
(Foder's)

SERIES A.								
1922					1923			
No.	TIME	CHURCH	WILSON	SHERWOOD	CHURCH	BAIER	BADOLLET	SHERWOOD
1	Immediate	Negative	Negative	Negative	Negative	Too dark to test	Negative	Too dark to test
	1 minute	Negative	Negative	Negative	Negative		Negative	
	5 minutes	Negative	Negative	Negative	Negative		Negative	
2	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Negative	Negative	Negative	Negative	Negative
3	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Too dark to test
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	
	5 minutes	Negative	Negative	Negative	Negative	Negative	Suspicious	
4	Immediate	Negative	Suspicious		Negative		Negative	
	1 minute	Negative	Positive	Too dark to test	Negative	Too dark to test	Negative	Too dark to test
	5 minutes	Negative	Positive		Negative		Suspicious	
SERIES B.								
1	Immediate	Negative	Negative	Negative	Negative	Too dark to test	Negative	Too dark to test
	1 minute	Negative	Negative	Negative	Negative		Negative	
	5 minutes	Negative	Negative	Negative	Negative		Negative	
2	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Negative	Negative	Negative	Negative	Negative
3	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Too dark to test
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	
	5 minutes	Negative	Negative	Negative	Negative	Negative	Suspicious	
4	Immediate	Negative	Negative		Negative		Negative	
	1 minute	Negative	Negative	Too dark to test	Negative	Too dark to test	Negative	Too dark to test
	5 minutes	Negative	Negative		Negative		Suspicious	
SERIES C.								
1	Immediate	Negative	Negative	Negative	Negative	xxxx	Negative	
	1 minute	Negative	Negative	Negative	Negative	xxxx	Negative	
	5 minutes	Negative	Negative	Negative	Negative	xxxx	Positive	Too dark to test
2	Immediate	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	1 minute	Negative	Negative	Negative	Negative	Negative	Negative	Negative
	5 minutes	Negative	Negative	Negative	Negative	Negative	Negative	Negative
3	Immediate	Negative	Negative	Negative	Negative		Negative	
	1 minute	Negative	Negative	Negative	Negative	Too dark to test	Positive	Too dark to test
	5 minutes	Negative	Negative	Negative	Negative		Negative	
4	Immediate	Negative	Negative		Negative		Negative	
	1 minute	Negative	Negative	Too dark to test	Negative	Too dark to test	Negative	Too dark to test
	5 minutes	Negative	Negative		Negative		Suspicious	
SERIES X.								
1	Immediate	Suspicious	Positive		Suspicious		Negative	
	1 minute	Suspicious	Positive	Too dark to test	Suspicious	Too dark to test	Negative	Too dark to test
	5 minutes	Suspicious	Positive		Suspicious		Suspicious	

that have been heated at temperatures that would prevail in the ordinary commercial handling of this product. Thus, it would appear to be true that a positive result with either test indicates the presence of commercial invert sugar sirup or, at least, of a foreign substance. Muttelet and Moroy<sup>1</sup> stated recently that the resorcin test (Fiehe's) affords negative results even in the case of honey that has been heated during the process of extraction.

<sup>1</sup> *Ann. fals.*, 1923, 16: 344.

These conclusions with regard to heated honey, however, appear to have been negatived within the past few days by results obtained by the associate referee working on portions of the 1922 samples. Every sample of each of the three series gave a distinctly positive reaction. The samples had been stored in sealed bottles for one year, and the positive reaction was obtained in each case upon initial and also upon repeated examination. These results are astonishing and surprising. It is obvious that the matter calls for extended investigation. Pending such investigation, the following conclusions are offered:

#### CONCLUSIONS.

The resorcin test (Bryan's modification of Fiehe's test) and the aniline chloride test (Feder's) afford reliable tests for indicating the presence of commercial invert sugar sirup in honey unless it can be shown that the honey has been stored for some length of time after having been heated to temperatures of upwards of 160° F. (71.7° C.).

The resorcin test may be applied to all types of honey, but the aniline chloride test is of no value in the case of dark colored honey.

The statement that a positive test consists of a bright red color is insufficient for the guidance of the analyst. It should be emphasized that a positive test consists of a cherry red color appearing at once and that yellow to salmon shades of color have no meaning.

#### RECOMMENDATIONS.

It is recommended—

(1) That further investigation be made relative to the application of the resorcin and the aniline chloride tests to honey that has been stored for varying lengths of time after having been heated to temperatures that would prevail in the ordinary commercial handling of the product.

(2) That the part of this report headed "Conclusions" be made a part of the *Book of Methods*.

No report on maple products was given by the associate referee.

THE LEAD NUMBER OF MAPLE PRODUCTS<sup>1</sup>.

By C. A. CLEMENS (State Food and Drug Laboratory, Vermilion, S. Dak.).

As alcohol is a reagent that must be used sparingly in many laboratories, any modification of a method that eliminates its use is worthy of note. To develop such a method, comparisons were made of values given by the Winton lead number on maple sirups when the lead was determined as sulfate, chromate, molybdate, or phosphate. In Table 1 results of analysis show that the chromate and molybdate methods gave concordant values, which were somewhat higher than the values given by the sulfate method. In other words, the sulfate method gives higher results for lead than does either the chromate or the molybdate method.

TABLE 1.  
*Winton lead number of maple sirups.*

LEAD DETERMINED AS—	ON SAMPLES AS RECEIVED						ON DRY BASIS					
	1	2	3	4	5	6	1	2	3	4	5	6
Sulfate . . . . .	1.70	1.67	1.70	1.73	1.94	1.56	2.61	2.47	2.59	2.58	2.99	2.38
Chromate . . . . .	1.79	1.84	1.83	1.91	2.22	1.73	2.75	2.72	2.79	2.85	3.43	2.64
Molybdate . . . . .	1.70	1.83	1.82	1.89	2.15	1.69	2.61	2.71	2.77	2.82	3.32	2.58

Several experiments were carried out to find the cause of these differences. The two components that seemed most likely to have an influence on the determination were sugar and potassium acetate. The lead was determined in various basic lead acetate solutions containing a few drops of acetic acid, and the results were used as the standard of comparison. The sulfate, chromate, and molybdate methods gave good checks under these conditions. To these solutions were then added cane sugar, potassium acetate, or mixtures of these two substances. The presence of the sugar caused no change in the quantity of lead obtained by any of the methods. When potassium acetate was present, the quantity of lead found by the chromate and molybdate methods was unaffected, but the quantity found by the sulfate method was increased when potassium acetate was present in sufficient quantity. When mixtures of sugar and potassium acetate were used, the increase in the amount of lead found was the same as though potassium acetate alone were present. It may be true that lead sulfate precipitates are contaminated in a manner similar to those of barium sulfate.

These results seem to indicate that one of the disturbing elements is potassium acetate, and that it interferes with the accurate determination

<sup>1</sup> Presented by W. Seaman.

of lead by the sulfate method as employed in the Winton lead number. A more detailed study of the effect of various substances on the determination of lead has been planned.

TABLE 2.  
*Ross lead number of maple sirups.*

LEAD DETERMINED AS—	ON SAMPLES AS RECEIVED						ON DRY BASIS					
	1	2	3	4	5	6	1	2	3	4	5	6
Sulfate.....	1.76	1.69	1.76	1.70	1.87	1.54	2.70	2.50	2.68	2.53	2.89	2.35
Chromate.....	1.82	1.83	1.81	1.88	2.02	1.69	2.79	2.71	2.76	2.80	3.12	2.58
Molybdate.....	1.82	1.81	1.77	1.88	2.07	1.68	2.79	2.67	2.69	2.80	3.20	2.56

TABLE 3.  
*Ross lead number on mixtures of maple and cane sirups.*

ON SAMPLES AS RECEIVED			ON DRY BASIS		
Sulfate	Chromate	Phosphate	Sulfate	Chromate	Phosphate
0.28	0.27	0.23	0.43	0.41	0.35
0.33	0.35	0.31	0.50	0.53	0.47
1.29	1.36	1.35	1.96	2.07	2.05
0.58	0.62	0.59	0.84	0.90	0.86
0.42	0.44	0.50	0.63	0.66	0.75
0.72	0.77	0.73	1.06	1.14	1.08
0.72	0.74	0.80	1.04	1.07	1.16
0.57	0.59	0.58	0.85	0.88	0.87
0.46	0.48	0.34	0.68	0.71	0.54
0.14	0.08	..	0.21	0.12	..
0.84	0.82	..	1.23	1.20	.
1.14	1.13	....	1.70	1.69	..
0.87	0.85	....	1.29	1.26	..

Determinations on the same sirups were made employing the Ross modification of the Winton lead number and similar results were obtained (Table 2).

As the Ross lead number is used quite generally in the estimation of the amount of maple sirup present in mixtures of maple and cane sirup, comparisons were made on a number of such sirups. The results are shown in Table 3.

The difference between the values given by the sulfate and chromate modifications of the Ross method on mixtures is so small that it is negligible in most cases. The phosphate modification is not so satisfying.

Five samples containing glucose were also run. The values obtained are shown in Table 4.

TABLE 4.  
*Ross lead number on glucose products.*

ON DRY BASIS					
METHOD	Glucose, sirup	Glucose, cane, and maple sirup	Glucose, cane, and maple sirup	Glucose, cane, and imitation maple sirup	Glucose, cane, and maple sirup
Sulfate . . . . .	1.18	2.17	1.12	1.31	1.04
Chromate . . . . .	1.09	2.11	1.06	1.21	0.94

The molybdate determination of lead offered many difficulties owing to the formation of colloidal solutions. Perhaps, after extended investigation, these difficulties might be overcome. The slow filtration of the phosphate solution and the variation in duplicates eliminate the phosphate method, at least until further investigation.

The chromate method gives excellent checks, is easily manipulated, and requires no more actual working time than does the sulfate method; it can be finished in less total time. The description of the procedure follows:

Prepare the filtrates as directed in the Winton or Ross lead numbers and use 10 cc. aliquots for the determinations.

To the filtrate in a 400 cc. beaker, add 40 cc. of water and 25 cc. of an approximately 0.1N potassium dichromate solution, followed by 2 cc. of glacial acetic acid. Boil the solution until the yellow precipitate turns to a shade of orange or red. (The yellow precipitate gives higher results since it is difficult to wash.) Quickly filter and wash the crystalline compound onto a tared Gooch crucible. (The filtrate should be yellow with excess dichromate.) Wash the precipitate with hot water, dry in an oven at 110° C. or in vacuo at the temperature of boiling water, cool, and weigh as lead chromate ( $\text{Pb CrO}_4$ ). The time of drying may be shortened by washing the precipitate with small portions of alcohol and ether and drying for one-half hour in a vacuum oven at the temperature of boiling water. The lead number is calculated by the following formula:

$$P = \frac{100 \times 0.64109 (S-W)}{2.5} = 25.64 (S-W), \text{ in which}$$

P = lead number (grams of metallic lead in the precipitate obtained from 100 grams of the sample);

S = grams of lead chromate corresponding to 2.5 cc. of the lead acetate solution as determined in a blank analysis; and

W = grams of lead chromate obtained from 10 cc. of the filtrate from the lead acetate precipitate.

#### SUMMARY.

A comparison of the sulfate method for the lead numbers in maple products with other methods, particularly the chromate method, shows that the sulfate method is unreliable. The chromate method is more rapid than the sulfate method and does not require the use of alcohol.

The presence of potassium acetate in a solution causes the sulfate method for lead to give results higher than the actual content.

#### REPORT ON MALTOSE PRODUCTS.

By H. C. GORE (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*

The work carried on during the past year consisted of attempts to obtain a purified and concentrated preparation on the enzyme maltase, with the idea of using such enzyme preparation as a reagent in the analysis of mixtures of maltose, dextrin, and dextrose, as outlined in last year's report<sup>1</sup>. This work has been of such a character that collaborative assistance was not necessary; it was done by the associate referee, assisted by F. W. Reynolds of the Carbohydrate Laboratory, Bureau of Chemistry. Substantial progress has been made, although the problem has not been solved.

The Willstätter and Steibelt method<sup>2</sup> of preparing maltose from fresh bottom yeast was employed. This method follows:

#### METHOD.

Eleven grams of yeast (corresponding to 2.5 grams of dry yeast) is mixed in a beaker with 1 cc. of ethyl acetate and rubbed with a glass rod from 4 to 6 minutes or until liquefaction is complete. Twenty cc. of water is then mixed in and 0.1N ammonia is added immediately, drop by drop, with vigorous stirring until a neutral reaction is obtained. This is tested for by using sensitive blue litmus paper and comparing the color with that given by distilled water. Litmus solution can also be used on a spot plate. From 7-9 cc. of the ammonia solution will be required. The mixture is allowed to stand for 10 minutes and, if necessary, again brought to neutrality; usually about 1.5 cc. more of the 0.1N ammonia will be required. The mixture is then transferred to a 50 cc. graduated flask and made up to the mark.

<sup>1</sup> J. Assoc. Official Agr. Chemists, 1923, 6:364.

<sup>2</sup> Z. physiol. Chem., 1920, 111: 168.



The maltase activity in the preparation of autolyzed yeast is determined as follows:

Withdraw 20 cc. (corresponding approximately to 1 gram of dry yeast) by a pipet and mix in a 100 cc. flask with a solution of 5 grams of C. P. maltose. Add 4 cc. of buffer solution, consisting of a mixture of equal volumes of a solution of  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , 6 grams per 100 cc. and a solution of  $\text{KH}_2\text{PO}_4$ , 4.5 grams per 100 cc., make up to 100 cc. with water, and incubate at  $30^\circ\text{C}$ . for an hour or similar determined interval. Take 25 cc. with a pipet, add 5 cc. of 2 N solution of sodium carbonate, filter, and polarize.

Correct the reading for dilution by the sodium carbonate solution.

The original reading of 5 grams of maltose in 100 cc. is then determined in the same manner.

The difference in the readings divided by the total change in polarization that would occur if the maltose were hydrolyzed completely gives the percentage converted.

#### EXAMPLE.

The rotation of a solution of 5 grams of C. P. maltose in 100 cc. (after destroying mutarotation in a 25 cc. portion by 5 cc. of 2N sodium carbonate and correcting for dilution) was  $37.43^\circ\text{V}$ . The rotation of the test portion (after correction for dilution by sodium carbonate) was  $30.72^\circ\text{V}$ . The fall in rotation was therefore  $6.71^\circ\text{V}$ . The total change in rotation, assuming that all the maltose became hydrolyzed, is  $22.18^\circ\text{V}$ .

Thus the percentage hydrolyzed was  $\frac{6.71}{22.18}$ , or 30.2.

Attempts to concentrate maltase by ultrafiltration have proved successful, and the principal difficulty now remaining to be overcome is that of apparent instability of the enzyme. In other words, it will be necessary to determine the nature of the destructive influences and devise means for controlling them.

It is recommended that work during the next year be continued along the same line.

### DETERMINATION OF TOTAL SOLIDS IN SUGAR-HOUSE PRODUCTS.

By J. F. BREWSTER (Louisiana Sugar Experiment Station, New Orleans, La.), *Associate Referee on Sugar-House Products*.

Five methods for the determination of total solids in sugar-house products, which comprise sirups, molasses, massecuites, etc., have been described in publications of this association and adopted as official<sup>1</sup>.

Two of the methods are for the direct determination of solids after driving off moisture by drying upon pumice stone at  $70^\circ$  in vacuo or upon quartz sand at the temperature of a boiling water oven.

The pumice stone method has been studied recently by Seidenberg<sup>2</sup>,

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 101.

<sup>2</sup> The Behavior of Pumice Stone During the Dehydration of Organic Liquids. *J. Assoc. Official Agr. Chemists*, 1923, 7: 98.

who shows why, in preparing the pumice for use, it should be heated to redness. He concludes that decomposition of organic matter distributed upon pumice is accelerated by moisture already adsorbed at comparatively low temperatures, but that it does not take place in dilute solutions.

The official method for drying upon sand is open to criticism from at least two points of view. First, the directions call for "6-7 grams of the prepared sand" and "3-4 grams of the molasses". It is difficult to say how the directions came to be so printed, for it has been the usual procedure everywhere, so far as the writer knows, to use 20-25 grams of prepared sand to about 1 gram of dry substance in the sample.

The sand-drying method was studied by Aikin<sup>1</sup>, who applied it to the examination of beet molasses. He recommends 25-30 grams of sand that will pass through a 0.25 mm. screen and states that still finer grains are satisfactory. His drying temperature was 105°.

The second objection to the official sand method is the long exposure to the temperature of the boiling water oven (about 95°) when dealing with cane products containing fructose. This temperature effect was discussed early by Carr and Sanborn<sup>2</sup>. In fact it was a result of their work that drying in vacuum at 70° was recommended in the pumice method.

Before leaving the subject of the determination of solids by drying, reference should be made to three newer methods or sets of apparatus that have been tried this year. These are the Brown-Duvel moisture tester<sup>3</sup>, the Spencer oven with the procedure described by Meade<sup>4</sup>, and the Seidenberg gauze dish<sup>5</sup>. These are more fully described later.

The densimetric methods by spindle and by pycnometer are open to the same well-known objection, namely, that correct results can not be obtained with solutions, such as sirups and molasses, that contain non-sugars whose specific gravities vary widely from those of the sugars. There are left the refractometric methods, which usually yield lower results when applied to impure solutions, such as sirups and molasses, than do the drying methods. This again is because the indices of refraction of the impurities vary from those of pure solutions of the sugars upon which the method is based.

To test the various methods samples were prepared as follows: artificial sirup, pure cane sirup, medium cane molasses, beet molasses, and fill-mass. All the methods described were used, and the results were contributed by the following collaborators, to whom the writer at this time desires to express his thanks: R. T. Balch, Bureau of Chemistry, Wash-

<sup>1</sup> *J. Ind. Eng. Chem.*, 1920, 12: 979.

<sup>2</sup> U. S. Bur. Chem. Bull., 47, 1896.

<sup>3</sup> U. S. Dept. Agr. Bull., 56; Bur. Plant Ind. Circ. 72: 1914.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1921, 13: 924.

<sup>5</sup> *J. Ind. Eng. Chem.*, 1915, 7: 769; 1923, 15: 737; *J. Assoc. Official Agr. Chemists* 1923, 7: 98.

ington, D. C.; C. H. Christman, 636 Fifth Avenue, Clinton, Iowa; K. R. Lindfors, Michigan Sugar Co., Saginaw, Mich.; I. H. Morse, New Orleans, La.; H. Z. E. Perkins, American Sugar Refining Co., New Orleans, La.; and Armin Seidenberg, Chemical Laboratory, Department of Health, New York.

#### METHODS USED.

The five official methods are so well known that only the changes in or additions to the text, which were made with the object of obtaining uniform procedure for the purposes of the present collaborative work, will be indicated.

##### *Drying upon Pumice Stone.*

Additions to the text of the official method were as follows: "Accurately dilute sample with twice its weight of water". Under the preparation of pumice a full description was lacking in the text; therefore, in addition to the preparation of the two sizes of granules it was directed to "digest (the sifted pumice) with dilute sulfuric acid (1:4), wash free of acid, and heat to redness".

##### *Drying upon Quartz Sand.*

Instead of "6-7 grams of the prepared sand", 20-25 grams were recommended. Instead of "3-4 grams of the molasses", 3-4 grams of the 1:2 diluted sample were recommended.

##### *Aerometric Methods: By means of a Spindle.*

Under "Aerometric Methods" a note explains that these methods are "not applicable to low-grade sugar products, molasses, and other materials containing large amounts of non-sugar solids", yet the method seems to be in very general use for the determination of total solids. The only addition to the directions was a recommendation to dilute a weighed portion of the sample with an equal weight of water for the determination and to calculate solids as percentage of the original sample.

##### *By Means of a Pycnometer.*

A change in the text of this method was a recommendation to use the 1:1 diluted sample and to calculate solids as percentage of the original material.

##### *Refractometer Method.*

Directions for the use of this method were changed to read "original sample" instead of "solution" in the first line of the text.

*Spencer Oven.*

Of the newer methods for the determination of solids or moisture, the Spencer oven, as used by Meade for the determination of solids in molasses, sirups, and juices, will be considered first. This method is as follows:

The capsule is filled with freshly ignited fluffy asbestos, loosely packed, and the whole is weighed. The capsule holds about 6 grams of asbestos. The liquid to be dried is run on the asbestos, drop by drop, in an amount not to exceed 4 cc., and the capsule, plus the sample, is again weighed. The air current of the oven is then turned on, and the oven is heated to 110° C., after which the capsule is placed in the oven; the temperature is again brought to 110° and maintained at that point throughout the heating period, while the full current of air is drawn through the sample. At the end of the period the electric current and the air are both shut off. The capsule is removed to a desiccator, cooled, and weighed.

Certain modifications of Meade's original procedure were recommended by R. T. Balch of the Bureau of Chemistry, the only collaborator reporting results with the Spencer oven. These modifications are as follows:

The woolly asbestos is best prepared by heating with water and then drying. In order to retain all fine fibres in the capsules when air is rapidly passing through them a thin pad of asbestos is put in the bottom, similar to the preparation of a Gooch crucible, and then the capsule is about three-quarters filled with the dry woolly asbestos, loosely placed upon the pad. The dishes are dried in the Spencer oven by passing air through them, from 10 to 20 minutes, at approximately 105° C., unless the heating of the sample is to be made at a lower temperature. The drying of asbestos and the sample should be done at the same temperature.

After cooling, the samples are weighed in a glass weighing bottle before and after the addition of the sample. The amount of material to be taken is dependent upon the product to be analyzed. Molasses and similar products should be double diluted so that the solids will not be much in excess of 40%. With sand drying it is customary to regulate the size of sample so that the solids will weigh approximately 1 gram. If this procedure is followed, the capsules containing the samples must be subjected to a preliminary drying at 105° C. from 40 to 60 minutes in a hot-air oven before placing in the Spencer oven, for otherwise a part of the solution would be sucked through and lost. To eliminate this preliminary drying, the sample taken can not be much in excess of 1 cc. With dilute solutions this might materially affect the accuracy of the determination.

The length of time for heating in the Spencer oven in order to bring the capsules to constant weight (within 0.1 per cent on solids; that is if the solids weigh 1 gram the loss on second heating should not exceed 0.001 gram) is approximately 45 minutes. A second heating of 10-15 minutes is but seldom necessary.

Solutions containing invert sugar can be analyzed in a similar manner, with the exception that the temperature for drying in the Spencer oven is not allowed to rise above 85° C.

Although the oven is not equipped with a thermoregulator, it would be a very desirable attachment when heating over such long periods of time. Without one, the oven needs considerable attention from the operator, who otherwise might be doing other work.

Determinations can be completely made in 3½ hours, whereas with sand drying the total time consumed is very close to 10 hours as a minimum. Duplicates check very closely by this method.

*Seidenberg Gauze Dish.*

This device was originally designed for the determination of solids and fats in such materials as condensed milk. Recently it has been somewhat modified by its inventor and recommended for use in the determination of solids in sugar products. The writer desires to express his indebtedness to Seidenberg for his hearty cooperation in supplying directions and information concerning the gauze dish. Description and directions are as follows:

The gauze dish is made from a fine-mesh wire gauze with an area of 200 sq. cm., corrugated into 31 to 33 lateral ridges and compressed in this way into an area of  $8.5 \times 5.5$  cm. Copper gauze may be used and should be slightly oxidized. In order to protect hygroscopic material it is placed during weighing in a closed dish made of thin, light-weight lead sheets. The drops of any liquid when delivered from a slight height (about 2 cm.) upon a gauze in this form are broken up by the impact of the fall and held entirely as a fine film within the meshes. In this way the grooves formed by the corrugations exert a capillary action and 5 cc. of any liquid can readily be distributed over the gauze dish without any going through the meshes.

The inventor recommends temperatures below  $60^{\circ}$  for substances containing levulose.

*Brown-Duvel Moisture Tester.*

No exact description of this apparatus was at hand when these directions were compiled, and only one collaborator signified his intention of using the method, which consists in distilling a weighed sample of material over xylene. The xylenes have boiling points ranging from  $138^{\circ}$ – $143^{\circ}$ , so that the water contained in the sample is carried over and on being collected with the distillate separates from the xylene, forming the heavier layer, which may be measured.

## RESULTS.

The results of determinations of total solids by the various methods are compiled in Tables 1–6.

The artificial sirup is the only material analyzed whose composition is known. Its calculated solid content is 66.90 per cent. The pumice method gave good results in the hands of three of the four analysts, although the range of error for separate determinations is wide; the lowest result, 66.58 per cent, and the highest, 68.19 per cent, differ from the theoretical by 0.32 and 1.29 per cent, respectively. The average of all the results, 67.11 per cent for the pumice method, differs from the theoretical by only 0.21 per cent. The sand method in the hands of three analysts, one of whom reported using a temperature of  $70^{\circ}$  and reduced pressure, furnished good results. The lowest results, obtained at  $105^{\circ}$ , demonstrated the effect of the higher temperature. The average

of the results with the gauze method are 1.69 per cent higher than the theoretical. This may be explained by the fact that the temperature recommended by the inventor of the gauze is too low to dehydrate completely the material at atmospheric pressure. This method appears to yield the highest results of all the drying methods as will be seen in the tables under analyses of other materials. The densimetric results are low and those by refractometer high.

TABLE 1.

*Total solids, artificial sirup.*

ANALYST	PUMICE	SAND	GAUZE DISH	SPENCER OVEN	SPINDLE	PYCNO- METER	REFRACTO- METER
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Balch . . . . .	66.54	65.92	....	66.20	.	..	..
	66.58	65.86	..	66.26	.	..	..
	66.60	65.94	..	66.28	67.60	67.52	66.12
Average . . . . .	66.57	65.91	..	66.25	67.60	67.52	66.12
Christman . . . . .	66.77	67.16	....	..	..	67.78	65.97
Lindfors . . . . .	.	.	..	.	.	..	65.94
Perkins . . . . .	67.00	67.04	..	..	..	66.60*	65.45
	67.11	66.96	..	..	..	67.80†	64.88‡
Average . . . . .	67.06	67.00	..	.	.	67.20	65.17
Seidenberg . . . . .	67.73¶	67.13	68.66	..	..	..	..
	68.19	..	68.60	.	.	..	..
	68.17	..	68.53	.	..	.	..
	..	..	68.64	..	..	..	..
	..	.	68.54	..	..	.	.
Average . . . . .	68.03	67.13	68.59	..	..	.	..
General Average	67.11	66.80	68.59	66.25	67.60	67.43	65.67

\*20°/4°.

†17.5°/17.5°.

‡Artificial sirup, 8.618 grams mixed with 10.072 grams of white sirup containing 79.25 % solids as sucrose.

¶Pumice prepared by heating 3 hours at 70°.

## COMPOSITION OF ARTIFICIAL SIRUP.

	<i>grams</i>
Sucrose . . . . .	402.00
Invert sugar . . . . .	261.78
Cane gum . . . . .	8.04
Sodium chloride . . . . .	1.17
Potassium chloride . . . . .	2.45
Potassium sulfate . . . . .	15.00
Total solids . . . . .	690.44
Added water . . . . .	341.56
Weight of sirup . . . . .	1032.00
Percentage of solids in sirup . . . . .	66.90

In the analysis of cane sirup, Table 2, fair agreement is found in the pumice method by two analysts. The general average is 70.72 per cent, with the highest result 70.98 and the lowest 70.55 per cent. The Spencer oven, reported by one analyst, yielded average results of 70.97 per cent, a difference of +0.25 per cent from the pumice average. The

TABLE 2.  
*Total solids, cane sirup.*

ANALYST	PUMICE	SAND	GAUZE DISH	SPENCER OVEN	SPINDLE	PYCNO-METER	REFRACTO-METER
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Balch.....	70.88	70.16	.....	70.90	...	...	.....
	70.98	70.12	...	70.94	...	...	.....
	70.80	70.12	...	70.96	...	...	.....
	70.88	70.22	71.81	70.94	...	...	.....
	70.60	70.06	71.78	71.12	72.60	72.34	70.67
Average.....	70.83	70.12	71.80	70.97	72.60	72.34	70.67
Morse.....	.....	.....	.....	.....	.....	72.03*	.....
Perkins.....	70.55	69.40	...	...	...	...	69.20
	70.66	70.31	...	...	...	...	69.67
Average.....	70.61	69.86	.....	.....	...	...	69.49
General Average.	70.72	69.99	71.80	70.97	72.60	72.19	70.08

\*Average of 17 closely agreeing determinations.

TABLE 3.  
*Total solids, medium cane molasses.*

ANALYST	PUMICE	SAND	GAUZE DISH	SPENCER OVEN	SPINDLE	PYCNO-METER	REFRACTO-METER
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Balch.....	75.98	73.86	75.66	75.26	...	.....	.....
	75.88	73.98	75.43	75.24	...	.....	.....
	76.34	73.16	...	75.54	...	.....	.....
	76.12	73.22	.....	76.58	81.20	80.93	75.80
Average.....	76.08	73.56	75.55	75.41	81.20	80.93	75.80
Christman.....	75.03	75.10	.....	.....	...	78.82**	76.35
Lindfors.....	...	.....	.....	.....	.....	.....	79.14**
Morse.....	...	.....	.....	.....	.....	80.60*	.....
Perkins.....	75.10	74.07	.....	.....	.....	.....	75.96†
	75.35	74.86	.....	.....	.....	.....	75.54†
Average.....	75.23	74.47	.....	.....	.....	.....	75.70
Seidenberg....	...	.....	77.14	.....	.....	.....	.....
	...	76.18	77.11	.....	.....	.....	.....
	70.00†	76.55	77.24	.....	.....	.....	.....
	75.39¶	75.64¶	77.12	.....	.....	.....	.....
Average.....	76.19	76.12	77.15	.....	81.20	80.77	75.96
General Average.	75.63	74.81	76.35	75.41	81.20	80.77	75.96

\*Average of 16 closely agreeing determinations.

†Molasses, 9.584 grams, mixed with white sirup, 12.239 grams.

‡Pumice heated to redness in preparation.

¶Heated 44 hours at 95°.

\*\*Omitted from averages.

TABLE 4.  
*Total solids, beet molasses.*

ANALYST	PUMICE	SAND	GAUZE DISH	SPENCER OVEN	SPINDLE	PYCNO- METER	REFRACTO- METER
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Balch . . . . .	80.04	78.86	.....	80.32	.....	.....	.....
	80.22	79.10	.....	80.32	.....	.....	.....
	79.96	.....	.....	79.94	.....	.....	.....
	79.90	79.30	80.32	79.80	.....	.....	.....
	80.00	79.12	80.24	79.94	81.80	81.60	78.40
Average . . . . .	80.02	79.10	80.28	80.06	81.80	81.60	78.40
Christman . . . . .	80.27	79.88	.....	..	..	..	79.50
Lindfors . . . . .	(Brown-Duvel	moisture	tester 79.90)	.....	.....	79.72*	78.93†
Perkins . . . . .	79.86	79.54	..	..	.....	81.50†	78.48†
	80.02	80.06	.....	.....	.....	.....	.....
Average . . . . .	79.94	79.80	..	..	..	80.61	78.71
General Average.	80.08	79.59	80.28	80.06	81.80	81.10	78.82

\*Determined at  $20^{\circ}$   
 $4^{\circ}$ .

†Determined at  $17.5^{\circ}$   
 $17.5^{\circ}$ .

‡Beet molasses, 7.043 grams, mixed with 15.504 grams of white sirup containing 79.25% solids as sucrose

TABLE 5.  
*Total solids, beet fillmass.*

ANALYST	PUMICE	SAND	GAUZE DISH	SPENCER OVEN	SPINDLE	PYCNO- METER	REFRACTO- METER
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Balch . . . . .	90.18	88.92	..	89.62	..	..	..
	90.38	88.76	..	89.74	..	..	..
	90.16	88.92	..	89.66	..	..	..
	90.24	88.62	91.08	89.70	..	..	..
	90.30	88.62	90.85	89.76	91.00	90.53	90.36
Average . . . . .	90.26	88.77	90.97	89.70	91.00	90.53	90.36
Christman . . . . .	88.91*	88.79	..	..	..	89.71	..
Lindfors . . . . .	(Brown-Duvel	moisture	tester 89.30)	.....	.....	.....	.....
Perkins . . . . .	90.47	89.87	.....	.....	.....	.....	.....
	89.88	90.28	.....	.....	.....	.....	.....
Average . . . . .	90.17	90.08	.....	.....	.....	.....	.....
Seidenberg . . . . .	91.18	87.48	.....	.....	.....	.....	.....
	90.89	.....	92.24	.....	.....	.....	.....
	91.28	.....	92.23	.....	.....	.....	.....
	90.95	.....	92.16	.....	.....	.....	.....
Average . . . . .	91.07	87.48	92.21	.....	.....	.....	.....
General Average.	90.50	88.78	91.59	89.70	91.00	90.12	90.36

\*Omitted from averages.



sand method gave average results lower, while the gauze dish gave figures higher than the pumice or the oven. The densimetric results are higher and the refractometric results lower than those of any of the drying methods.

Some variation among analysts and wide variations among methods are found with medium cane molasses, Table 3. If the different methods are considered on the basis of averages of results by all the analysts close agreement is found between the pumice and Spencer oven methods, the difference being 0.22 per cent. The sand method gives lower and the gauze dish higher results than either of these. However, one analyst obtained with the gauze dish an average of 75.55 per cent at temperatures 60°–65° against 75.63 per cent, the average for pumice, and 75.41 per cent for the oven. The other analyst reporting on the gauze and employing temperatures of 48°–56° obtained results averaging 77.15 per cent. The densimetric and refractometric methods exhibit their usual tendencies.

In the analysis of beet molasses, Table 4, good agreement is found in the results obtained by the pumice, gauze, and Spencer oven methods. The sand results are somewhat low as compared with these, although the differences in the averages are not so great as those found in the analysis of the cane products. The densimetric results are higher and the refractometric results lower than those obtained by drying.

The results for fillmass, Table 5, offer difficulties in drawing comparison. There is disagreement among analysts and among methods. The averages found by two of the four analysts reporting on the pumice method agree acceptably well. If the general averages obtained by all the analysts are compared it will be observed that each average varies from the one next greater by about 1 per cent.

TABLE 6.  
*Comparison of averages.*

METHOD	ARTIFICIAL SIRUP	CANE SIRUP	MEDIUM MOLASSES	BEET MOLASSES	BEET FILLMASS
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Pumice, 70° . . . . .	67.11	70.72	75.63	80.08	90.50
Sand, W. B . . . . .	66.80	69.99*	74.81*	79.59	88.78*
Seidenberg Gauze Dish . . .	68.59	71.80	76.35	80.28	91.59
Spencer Oven . . . . .	66.25	70.97	75.41	80.06	89.70
Mean . . . . .	67.19	71.16	75.79	80.00	90.59
Densimetric . . . . .	67.22	72.32	80.99	81.69	90.56
Refractometer . . . . .	65.67	70.08	75.96	78.82	90.36
Mean . . . . .	66.45	71.20	78.48	80.26	90.46
Solids calculated . . . . .	66.90	.....	.....	.....	.....

\*Not included in averages.

It has recently been pointed out to the writer by C. A. Browne, that there is a possibility of the mean of the results for solids, obtained by the pycnometer and by the refractometer, closely approximating the solids as found by drying. To test this possibility, Table 6 was arranged, the mean of the averages for drying being separated from the averages by the densimetric and refractometric methods. Excellent agreement is shown under the column headed cane sirup and good agreement under beet molasses and fillmass. The agreement is not so good in the case of the artificial sirup, while there is wide disagreement in the averages for cane molasses.

Although more results than are reported at this time would be desirable, it is believed that these will serve as a guide for future work along this line.

In a review of the tables the effect of variation of drying temperature becomes apparent; it is noticed not only in the results of the different analysts but also in the averages for particular methods and is found to apply to the beet as well as to the cane products. If the averages, as shown in Table 6, represent a close approximation to the true dry solids it is apparent that the pumice method at 70° most frequently yields results that closely approach the average. It is followed in order by the Spencer oven, the gauze dish, and the sand method. The sand method yields results throughout that are too low, while the gauze-dish method gives results somewhat high. There can be little doubt that these disagreements are due primarily to differences in temperatures and pressures used in the desiccation.

It is to be inferred, therefore, that if uniform procedure in respect to temperature and pressure of desiccation be adopted for the pumice, gauze-dish, and sand methods, more nearly uniform results should be obtained. The Spencer oven has given results somewhat lower than the averages. Here a relatively high temperature, 105°–110°, was employed, but the time of exposure, compared to the other drying methods, is extremely short (45 minutes). With this method it is necessary, no doubt, to standardize temperature and time as well as rate of flow of the air current.

#### RECOMMENDATIONS.

It is recommended—

(1) That the procedure outlined in the method for drying upon pumice stone be retained at present as described, but that the following provision for the digestion of the pumice with acid when it is being prepared be inserted after the second sentence of the directions: "Digest with 2 per cent sulfuric acid 8 hours on the steam bath. Wash free of acid and heat to dull redness (about 425°)".

(2) That in the directions for the sand method the text be changed in the first sentence to read: "20-30 grams of the prepared sand" instead of the "6-7" as now printed. That the third sentence be changed to read somewhat as follows: "Then add sufficient of the diluted sample to furnish approximately 1 gram of dry solids and dry in vacuo at 70° to constant weight, making trial weighings at intervals of 2 hours".

(3) That a uniform procedure for the dilution of the original sample, preferably the so-called double dilution (1 part sample to 1 part water by weight) be adopted for trial in future collaborative work.

(4) That the collaborative work on the determination of total solids be continued.

## A POLARIMETRIC METHOD FOR THE ESTIMATION OF DIASTATIC POWER.

By H. C. GORE (Bureau of Chemistry, Washington, D. C.).

At present the most widely used methods for the estimation of diastatic power are based on the determination of copper reduction through the use of Fehling's solution. Such methods are inevitably cumbersome. Thus, if working by the standard Lintner<sup>1</sup> method as described, for instance, by A. J. Brown<sup>2</sup> or by Jago and Jago<sup>3</sup>, it is difficult for the analyst to complete more than six determinations in a day. It is the purpose of this paper to show that the use of the polariscope affords a far shorter and more convenient method.

Soluble starch has a high specific rotatory power, ranging from 190° to 200° C. Solutions of soluble starch containing 2 grams in 100 cc. are transparent and when undergoing digestion by malt diastase have been shown by H. T. Brown and co-workers<sup>4</sup>, to decline in polarization at rates proportional to the increases in copper reduction. The early work of Brown and Heron, however, showed that when the digestion of starch by diastase occurred in the cold, the usual close relation between the fall in polarization and the increase in reducing power was not observed, but the decrease in polarization was *greater* than was accounted for by the increase in reducing sugars. Brown and Morris later showed that this was due to the fact that the sugars freshly formed from the starch at ordinary temperatures existed in the low rotating form. By adding a little concentrated solution of ammonia, the mutarotation was rapidly destroyed and the polarizations were increased to the calculated values. As these authors did not have in mind a polarimetric method for the

<sup>1</sup> *J. prakt. Chem.*, 1886, 34: 378.

<sup>2</sup> *Laboratory Studies for Brewing Students*, p. 53. Longmans, Green and Co., 1904.

<sup>3</sup> *The Technology of Breadmaking*, p. 823. Simpkin, Marshall, Hamilton, Kent and Co., 1911.

<sup>4</sup> *J. Chem. Soc.*, 1879, 35: 596; 1895, 67: 300.

estimation of diastatic power, it is necessary to develop the conditions whereby the diastatic power can be estimated from the polarization declines. Accordingly, after a number of preliminary trials, the following experiment was made:

A solution of Lintner's soluble starch containing 2 grams of air dry starch per 100 cc. was prepared by mixing the calculated weight with cold water, pouring the mixture into a large volume of boiling water, boiling for a few minutes, cooling, making up to volume, and filtering. An infusion of malt was prepared by digesting 25 grams of pale distiller's malt with 500 cc. of water at room temperature for an hour, with constant stirring, and filtering with suction.

The initial polarization of a mixture of 100 parts of the starch solution and one part of the solution of diastase was determined by mixing 50 cc. of starch solution with 0.5 cc. of concentrated ammonia solution and 0.5 cc. of the diastase solution mixed in the order named, and polarizing at 20°–21° C. in a 4 decimeter tube. The reading was then multiplied by 1.01 to correct for the volume of ammonia used. The reducing power of the mixture of starch solution and malt infusion was determined by adding 25 cc. portions of the starch solution directly to Fehling's solution and then 0.25 cc. of diastase solution. The determination was completed by the Munson and Walker method<sup>1</sup>.

The temperature of 900 cc. of the starch solution was adjusted to 21° C. The solution was then mixed with 9 cc. of diastase solution and maintained at 21° C. throughout the experiment. Portions were removed at half-hour intervals and analyzed. The polarizations were observed before and after the destruction of the mutarotation, which was accomplished in each case by adding 0.5 cc. of strong ammonia to 50 cc. portions. The mixture was allowed to stand for 25 minutes before making final readings, this period of standing having been found to be sufficient for the polarizations to become constant. The final readings were corrected for the volume of ammonia used. Reducing sugar was determined by the Munson and Walker method, the samples taken being added directly to Fehling's solution.

The results are shown in Table 1 and in Figure 1.

TABLE 1.

*Fall in polarization and sugar formed during digestion of soluble starch by diastase.*

INTERVAL	POLARIZATION		MALTOSE FORMED	TOTAL POLARIZATION CHANGE
	°V.*	°V.†		
<i>Hours</i>			<i>grams per 101 cc ‡</i>	°V.
0	39.75	39.75	...	...
½	38.35	38.58	0.200	1.17
1	37.20	37.57	0.385	2.18
1½	36.25	36.76	0.356	2.99
2	35.50	35.90	0.674	3.85
2½	34.60	35.25	...	4.50
3	33.95	34.59	0.912	5.16

\*Polarization before destruction of mutarotation.

†Polarization after destruction of mutarotation.

‡The reducing sugar present in the original mixture calculated as maltose was 0.077 gram per 101 cc.

<sup>1</sup> *J. Am. Chem. Soc.*, 1906, 28: 663; 1907, 29: 541.

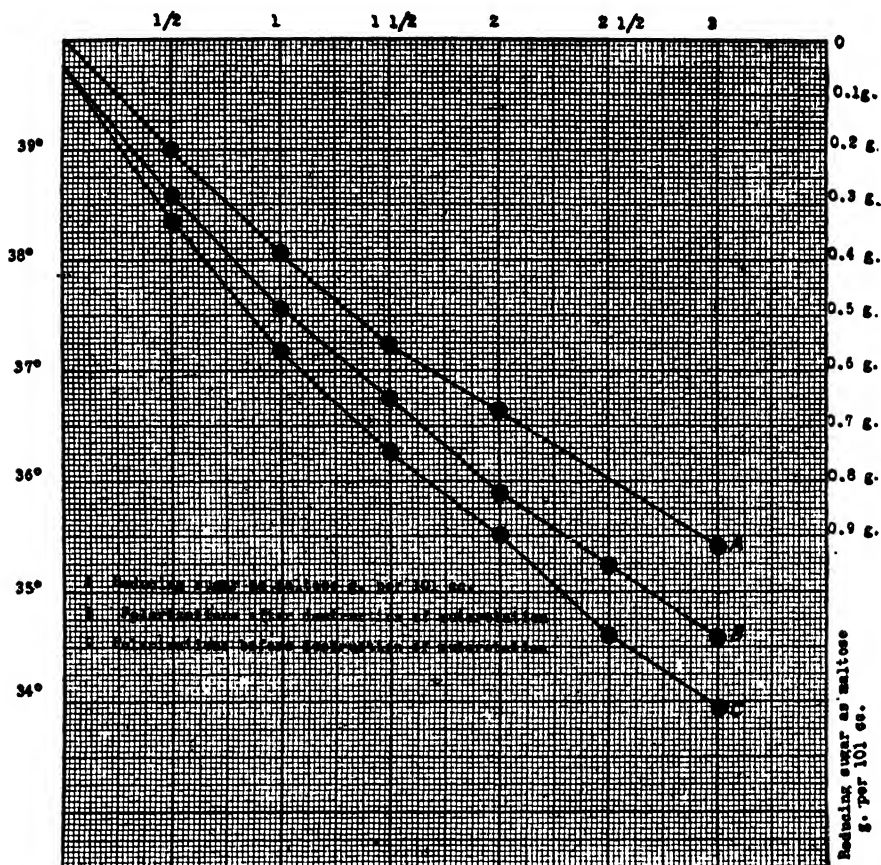


FIG. 1. FALL IN POLARIZATION AND SUGAR FORMED DURING DIGESTION OF SOLUBLE STARCH BY DIASTASE

The curve showing the reducing sugar formed, calculated as maltose in terms of grams per 101 cc., is similar to the curves shown by Kjeldahl<sup>1</sup>. The two curves representing polarization changes before and after destruction of mutarotation are slightly divergent, showing that the quantity of mutarotating sugar increases as the sugar is formed from starch.

The increase in reducing sugars formed during the first hour, expressed in terms of cuprous oxide, was 0.490 gram per 101 cc. of mash. Thus the activity of the diastase infusion, within experimental error, was equal to that of an extract of a malt of 100 Lintner, since the Lintner value by definition is 100 when one cubic centimeter of malt infusion prepared as specified by Lintner produces enough sugar to reduce com-

<sup>1</sup> *Compt. rend. trav. lab. Carlsberg*, 1879, 1: 109.

pletely 50 cc. of Fehling's solution in one hour at 21° C. This is equivalent to the formation of 0.4965 gram of cuprous oxide. The Lintner malt scale can therefore be related to the polarization decline observed, 2.18° V., by the following formula:  $L = \frac{100 d}{t \times 2.18}$ , where  $L$  is the activity on the Lintner scale,  $d$  is the observed fall in polarization,  $t$  is the time in hours, and 2.18 is the drop in polarization observed in a 4 decimeter tube produced by one cubic centimeter of a diastase solution representing 50 milligrams of a malt of 100° Lintner acting on 100 cc. of a starch solution containing 2 grams in 100 cc. for one hour at 21° C.

In the event that the results are to be expressed on Lintner's diastase scale instead of on the Lintner malt scale, the one cubic centimeter portion of the diastase solution should be so prepared as to represent 1.2 milligrams of the preparation of diastase being tested.

The method for the estimation of diastatic activity from the fall in polarization can be stated as follows:

Prepare a solution of Lintner's soluble starch containing 2 grams of air dry starch per 100 cc. and an infusion of the diastatic product to be tested of such concentration that one cubic centimeter corresponds to 50 milligrams of sample.

Determine the initial polarization of the mixture of starch and diastase solutions by mixing 50 cc. of the starch solution with 0.5 cc. of concentrated solution of ammonia and 0.5 cc. of the diastase solution in the order named, and polarize at 20°-21° C. in a 4 decimeter tube.

Adjust the temperature of 100 cc. of the starch solution to 21° C., add one cubic centimeter of the diastase solution, mix well, and let stand at 21° C. for a measured interval. This interval should be so chosen that the fall in polarization is not greater than 3° V. Withdraw a sample of 50 cc., add 0.5 cc. of strong ammonia, let stand for 25 minutes, and polarize in a 4 decimeter tube at 20°-21° C. Subtract the reading from the initial polarization and calculate by the formula here given. If the fall in polarization is very small, the remaining solution may be digested for a longer period, which can be calculated readily from the fall in polarization first observed.

*Example.*—An extract of a sample of wheat flour was tested by this method. The initial polarization was 38.35° V. The polarization of duplicates after one-half hour was 38.05° and 38°. The polarization after 3 hours was 36.05 and 36, respectively. The Lintner value as calculated by this method was 35.2 and 35.9.

#### COMMITTEES NAMED BY THE PRESIDENT.

*Committee on nominations:* F. P. Veitch of Washington, D. C., C. H. Jones of Vermont, and B. B. Ross of Alabama.

*Committee on resolutions:* R. N. Brackett of South Carolina, P. S. Burgess of Rhode Island, and J. W. Kellogg of Pennsylvania.

*Auditing committee:* G. L. Bidwell of Washington, D. C., C. S. Cathcart of New Jersey, and J. J. T. Graham of Washington, D. C.

*Committee to wait upon Secretary of Agriculture:* W. A. Withers of North Carolina, A. G. McCall of Maryland, and H. H. Hanson of Delaware.

*Committee to wait upon Honorary President:* W. F. Hand of Mississippi, J. K. Haywood of Washington, D. C., and C. C. McDonnell of Washington, D. C.

## FIRST DAY.

### MONDAY—AFTERNOON SESSION.

*C. A. Browne:* MR. CHAIRMAN AND FELLOW MEMBERS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS:

Although formerly active in the work of this association, I have not had an opportunity to attend any of its meetings for the past six years. It is, therefore, a great pleasure for me to see so many of my former co-workers and to attend a meeting of the organization to which I owed so much when I began my work in agricultural chemistry.

My interest in agricultural chemistry dates back about thirty years, when I was employed in a laboratory in New York City, and Dr. Wiley's "Agricultural Analysis" first came to my notice. As perhaps you know, this work was appearing at that time in installments, and the successive chapters were awaited by chemists with all the eagerness that attends the monthly reading of a serial. Sometime after this, when I became associated with William Frear of the Pennsylvania State College, my interest in agricultural chemistry was still further intensified. Dr. Frear was a very loyal member of this association, and one of the first duties that he assigned to me was in connection with its referee work. This was brought to my attention a short time ago when, in packing some of my old papers before moving to Washington, I found among them a referee's table of the cooperative work upon nitrogen. This old report, going back 27 years, contains the first work that I did for this association. It is interesting to note that of the sixteen collaborators mentioned in this report practically one-half afterwards became presidents of this association. Of this number, four have passed away. Of the others, I think perhaps six or seven, including myself, are present at this meeting.

As a result of my own experience, I should like to impress, particularly upon the younger chemists, the great value of this collaborative work. The training that the chemist acquires in testing out new methods is most valuable, and the comparison of his results with those of other chemists gives a better opportunity to gage his capacity as a chemist than is afforded in any other way.

It was remarked by one of the old referees—I think it was Street—that the purpose of this collaborative work is to test methods and not chemists. But the other point—that in testing methods we are also having a most excellent opportunity of testing ourselves—should not be minimized. The disagreement of chemists in a great many instances has been traced to a difference in the interpretation of language, and



the thought has been expressed that the phraseology of our methods should be such that it may be absolutely fool-proof. An excellent means, I think, of testing the wording of a method is to employ it in the instruction of students. If there is any deficiency in the meaning, it will certainly then become apparent. I remember how this was impressed on my mind in a rather peculiar way many years ago when I taught agricultural analysis and was using the methods of the A. O. A. C. as a textbook. The method stated that a particular substance was to be dissolved in a covered beaker, and that after washing off the cover glass it was to be evaporated to dryness. One of the students took this to mean that the cover glass was to be evaporated to dryness and not the contents of the beaker and acted accordingly. Many similar experiences might be enumerated. No doubt, in many cases, the wording of our methods could be improved.

The successful operation of our methods has been found in various instances to be due to some peculiar little point in sampling or technique upon which our instructions are silent. This should be corrected. Whether we should go beyond this is a matter upon which there may well be a difference of opinion. The point has been raised that our association should give more attention to research and less to analytical methods. While it is true, no doubt, that we, as chemists, are employed in research as well as in law enforcement work, and while it is also true that the end is more important than the means, it is impractical for us to depart too far from the purpose for which our organization was founded. As a society, we have always placed most stress upon the accuracy of our methods. A chemist must be a good analyst before he can become good in research.

Before concluding my remarks, I should like to announce that the doors of the Bureau of Chemistry are always open to the members of the association. The contact between this association and the Bureau has been very close from the beginning, and our chemists will be pleased to have any of you visit their laboratories.

### REPORT ON FERTILIZERS.

By R. N. BRACKETT (Clemson Agricultural College, Clemson College, S. C.), *Referee*.

Reference to the report of Committee A on Recommendations of Referees<sup>1</sup> at the last annual meeting of this association will show that the Bartlett distillation method for total boron in fertilizers was approved as official, first action, and that similar action was taken on the Ross-Deemer method for water-soluble boron in fertilizers. No further work was recommended on this subject. These two methods, of course, come up at this session for final action.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 258.

The method of preparation of ammonium citrate, as proposed by C. S. Robinson, was recommended by Committee A and approved as official, first action. No further work was recommended on this subject. This method also comes up for final action as an official method at this meeting.

The recommendations of Committee A on nitrogen, which were approved by the association, have not been carried out, because it has been impracticable to do so. These recommendations were: First, that the referee be instructed to study the Devarda method as applied to the nitrates of commerce; second, that the Moore method for nitrates be studied with collaborators; third, that the referee for 1923 be instructed to study the use of sodium thiosulfate as a substitute for sodium or potassium sulfide in the Kjeldahl method.

The General Referee on Fertilizers was, upon the recommendation of Committee A, approved by the association, instructed to "study the literature with regard to the use of alcohol stronger than 80 per cent for washing the potash precipitate with a view to ascertaining if collaborative investigation of the question is desirable". This report has been prepared and will be found on page 382.

The method for determining insoluble phosphoric acid in precipitated phosphates was adopted as official, final action, at the last convention.

The tentative Wagner method for determining citric acid-soluble phosphoric acid in basic slag phosphates was adopted as official, final action, at the last convention.

The following matters have been brought to the attention of the general referee since the last annual meeting:

*Nitrogen.*—A paper by E. W. Magruder (F. S. Royster Guano Co.) that had been read before the Fertilizer Division of the American Chemical Society at the Pittsburgh meeting, entitled "A Review of Methods of Determining Nitrogen in Fertilizers" by H. C. Moore (Armour Fertilizer Works). As promised, this paper is now brought to the attention of the members. The chief point in this paper is the suggestion that one method be adopted for fertilizers containing nitrates and one method for fertilizers without nitrates. The general referee does not recommend that this suggestion be adopted, and is prepared to give his reasons if the suggestion is taken up for discussion.

*Insoluble Phosphoric Acid in Double Super-Phosphates.*—A letter of July 19, 1923 from C. Clifton Howes, chemist of the Davison Chemical Co., Baltimore, Md., written at the suggestion of R. W. Balcom. This letter concerned a deviation from the procedure given in the *Book of Methods* for the determination of insoluble phosphoric acid. A quotation of two paragraphs from the letter will make the point clear:

We have found that due to the mechanical drying, the material is somewhat harder and drier than usual and the regular analytical scheme of transferring the weighed

2 gram portion to a 9 cm. filter has been preceded by thorough trituration with a little water in an agate mortar before washing, until 250 cc. have passed through the filter. The residue on the filter is then treated with neutral ammonium citrate and the official method followed.

By strictly following the official methods we were unable to obtain results that checked, but by the slight modification before mentioned good results were obtained.

At the request of R. E. Doolittle, Chairman, Committee on Editing Methods of Analysis, A. O. A. C., the general referee has suggested a number of changes in revision of Chapter I, Fertilizers, *Book of Methods*. As some of these changes call for approval by the association, they have been submitted to Committee A for consideration and action.

### REPORT ON BORAX IN FERTILIZERS.

By J. M. BARTLETT (Agricultural Experiment Station, Orono, Maine),  
*Associate Referee.*

The report of the referee on borax will be brief inasmuch as no work on this subject has been done by him during the past year. The association has voted to make the two methods suggested in previous reports official for the determination of borax in mixed fertilizers and fertilizer materials, and these methods come up this year for final action.

The object of the work done last year was to show that while the distillation method determines the boron soluble in very weak acids as well as that soluble in water, it actually determines only that which is injurious to plants, as was shown by vegetation experiments carried out in pot experiments in the greenhouse. It was found that in two of the minerals used in the experiments, only about one-third of the boron was soluble in hot water, while all of it was soluble in weak acid, and that these minerals proved to be just as injurious to the plants grown as like quantities of boron in borax with which they were compared. Consequently the referee made his second recommendation last year as follows: "It is recommended that in using the Ross-Deemer method for the determination of boron in fertilizer materials known to contain boron compounds not soluble in water but soluble in weak acids, sufficient hydrochloric acid be added to make the 50 cc. of water used in the first digestion on the steam bath to bring the boron into solution distinctly acid throughout the digestion".

This slight modification was recommended so that the two methods might agree on all kinds of materials, but Committee A did not think it wise to adopt it without further study. Owing to lack of time and materials the referee has not been able to carry the work farther this year, and under present conditions it hardly seems worth while for the association to spend more time on this subject. So far as the writer

knows, boron occurs in fertilizer materials only as the compound borax, and since the possibility of such minerals as Howlite and Colemanite, which were used in last year's experiments, getting into such materials is somewhat remote, the users of fertilizers would seem to be amply protected with the two methods as they are being adopted. The referee recommends, therefore, that the Ross-Deemer and Bartlett distillation methods be adopted in their present form.

No report on the Preparation of Ammonium Citrate was made by the associate referee. The general referee read the revised method for the preparation of neutral solutions of ammonium citrate<sup>1</sup> to be used in the determination of citrate-insoluble phosphoric acid and recommended that it be adopted as official.

## THE INTERPRETATION OF RESULTS OF THE ANALYSIS OF FERTILIZERS BY THE PERMANGANATE METHOD FOR DETERMINING THE ACTIVITY OF ORGANIC NITROGEN<sup>1</sup>.

By C. S. ROBINSON (Michigan Agricultural College, E. Lansing, Mich.).

This report is the outcome of a demand for a unification of the various ways of interpreting the results of the determination of the quality of organic nitrogen in fertilizers.

In connection with this problem the associate referee sent letters of inquiry to chemists in 38 States and received 24 replies. Thirteen chemists did not determine availability, nine used the alkaline method alone, three used the neutral method alone, and three used the alkaline, followed by the neutral in doubtful cases.

A survey of the schemes for interpreting the analytical data reveals that though there is a desire adequately to protect the consumer and at the same time allow the producer to utilize the organic sources of nitrogen, the manner of accomplishing this end varies greatly.

Seven laboratories examine only those materials whose contents of insoluble nitrogen exceed certain minimum values. These minimum values vary from 0.2 to 0.4 per cent insoluble nitrogen in five cases, while in two cases materials having less than 40 per cent of their nitrogen in the water-insoluble form are not tested.

Of the laboratories using the alkaline method only, three report simply the "per cent available", that is, the sum of the "water soluble" and the "active insoluble"; five give a passing grade to those samples showing 50 per cent or more of the insoluble nitrogen in the active form; while one requires that 75 per cent of the nitrogen shall be "available".

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<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 6: 390.

<sup>2</sup> Presented by C. H. Jones.

One of the laboratories using the neutral method, reported only the "per cent available"; one required that 85 per cent of the insoluble nitrogen be active; and one sets a limit of 75 per cent activity for mixed and 85 per cent activity for unmixed goods. Of those using both methods two required 50 per cent of the insoluble nitrogen to be active as determined by the alkaline method. In case of doubt one of these demanded a passing grade of 80 per cent by the neutral method, while the other fixed 85 per cent as the minimum. The third laboratory required a passing grade of 55 per cent activity by the alkaline or 80 per cent activity by the neutral method.

In this connection attention must be called to the question of the accuracy of the methods involved. It must be borne in mind that they are not capable of giving results as accurate nor as easily duplicated as the usual quantitative methods. The collaborative work of the association<sup>1</sup>, carried out in studying the methods prior to their adoption, shows that the agreement in the figures obtained by different analysts is not good, although most chemists agree that the same analyst can secure reasonably satisfactory checks.

It appears from the results cited that variations of 20 to 30 per cent in terms of activity are quite common, although the usual differences are only about half as large. It would seem that this represents the magnitude of error with careful work.

In reply to the question by the writer regarding the accuracy of the procedure, four collaborators answered that they allowed a variation of half a per cent; two stated that, in their own laboratories, results usually checked within 0.02 to 0.10 per cent but that they thought these limits would be exceeded when results from different laboratories were considered; and one placed the probable variation as 1 per cent and 2 per cent, respectively, when the work was done by the same or different workers. It is not within the scope of the present report to discuss the reasons for this situation, but its existence must be recognized and considered in any discussion of the interpretation of the results.

At present the difficulty is overcome by allowing a passing grade low enough to avoid injustice to the manufacturer.

In considering the interpretation of the results obtained by the official methods for evaluating the organic nitrogen in fertilizers another fundamental fact must be borne constantly in mind. It has been emphasized repeatedly by the authors of the methods and by subsequent investigators; nevertheless, it is still overlooked by many called upon to use the methods in question.

In regard to it, the associate referee can do no better than to quote from a paper by Hartwell and Pember<sup>2</sup>:

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<sup>1</sup> *J. Assoc. Official Agr. Chem.*, 1915, 1: 19, 385.

<sup>2</sup> *Ibid.*, 1923, 7: 55.

Among the methods of the A. O. A. C. are two official methods for determining the *active* water-insoluble nitrogen of fertilizers; one is frequently called the neutral and the other, the alkaline permanganate method. It has not been officially claimed, nor should it be claimed, that availability is determined by either one of the methods. The term "availability" conveys the conception that reference is made to the percentage available to crops; whereas, as has been stated, these methods for determining activity are incapable of furnishing definite information concerning availability. They simply attempt to separate, by the acceptance of arbitrary standards, not the good from the poor, but the better from the poorer quality of insoluble nitrogen, and it is not known that their authors make any greater claims for them.

In other words, the methods are fundamentally qualitative and not quantitative in character.

A study of the question shows that two questions must be answered, *viz.*, Who shall interpret the results of analysis? and, What basis shall be used for such interpretation?

In the first case there are two possibilities. The chemist may interpret his own results and report his judgment under the simple terms "passed" or "inferior". Or he may publish the actual figures with or without an explanatory statement as to the value of the material and leave the readers to interpret them as best they can. These figures may be given in terms of active and inactive insoluble nitrogen or as total available, *i. e.*, the sum of the water soluble and active insoluble.

In considering this second question attention is recalled to the necessity of keeping clearly in mind the qualitative limitations of the methods used which condemn the expression mentioned above wherein the total available nitrogen consisting of the sum of the water soluble and active insoluble is reported. Again quoting from Hartwell and Pember:

The word "activity" is suitably indefinite. It, instead of "availability", should always be used when referring to the chemical methods, and should be accompanied by the name of the particular method employed. Fifty per cent activity, for example, by the alkaline method, should never be interpreted to mean that half of the insoluble nitrogen is as available to the crops as that in nitrate of soda; yet many people still persist in making such an interpretation. It is more probable that less than a quarter of it is available. Fifty per cent activity is sometimes considered as the dividing point between better and poorer quality, but it should not be assumed that material registering 70 per cent activity is necessarily any more available than material with an activity of 60 per cent. It simply means that a larger proportion of its nitrogen was distilled from the alkaline permanganate solution, and that both may be included in the better group.

The investigations on these methods have not shown that material ammonified by permanganate is "available", nor even that organic nitrogen soluble in water is "available". It is not the separate amounts of active insoluble and inactive insoluble nitrogen that determine the value of a product; it is the relationship between the two.

Summing up the situation, it appears that the only interpretation possible is a general statement of the quality of the organic material.

Some plan necessarily should be adopted to indicate the importance of the organic nitrogen in the material involved to avoid discriminating against really high grade goods containing inconsequential amounts of organic material.

It is recommended, therefore, that the results of the determination of activity of organic nitrogen be interpreted as follows:

a. The methods shall be used only on materials containing insoluble nitrogen in excess of a minimum amount to be determined by the association.

b. Samples showing an activity of over 55 per cent by the alkaline method or 80 per cent by the neutral method shall be classed as "satisfactory"; those showing activities below this figure shall be classed as "inferior".

The chairman referred the preceding paper to the Committee on Definition of Terms and Interpretation of Results on Fertilizers.

### FLORIDA FERTILIZER LAW.

By R. E. ROSE (Chemical Division, Agricultural Department, Tallahassee, Fla.).

A problem has been presented to the State Laboratory of Florida involving a definition of "available" and "insoluble" ammonia in mixed commercial fertilizer containing organic and inorganic nitrogenous materials.

A recent statute adopted by the Legislature of Florida requires the manufacturer of commercial fertilizers to guarantee under oath that mixed fertilizer, or fertilizer material sold by him, shall be as follows:

#### BE IT ENACTED BY THE LEGISLATURE OF THE STATE OF FLORIDA:

\* \* \* Every package of commercial fertilizer or fertilizer material manufactured, imported, transported, distributed, stored, kept or offered for sale or sold in or into the State of Florida shall have securely attached a tag on which shall be plainly and legibly printed or written in ink the name or brand of the commercial fertilizer or fertilizer material; the name and address of the manufacturer or jobber; the net contents of the package in pounds; the chemical analysis stating the minimum percentages of available ammonia, insoluble ammonia, available phosphoric acid, insoluble phosphoric acid, water-soluble potash and total plant food; the maximum percentage of chlorine and moisture; and a statement of all the materials from which the commercial fertilizer or fertilizer material is made. There shall also be attached to the tag the stamp showing the payment of the fee required by law. There shall be no other statements on the tag.

\* \* \* The form for the tag shall be as follows:

Name or brand of fertilizer,  
Name of manufacturer or jobber,  
Address of manufacturer or jobber,  
Net weight in pounds.

#### GUARANTEED ANALYSIS.

Available ammonia, not less than.....	per cent
Insoluble ammonia, not less than.....	per cent
Available phosphoric acid, not less than.....	per cent
Insoluble phosphoric acid, not less than.....	per cent
Water-soluble potash, not less than.....	per cent
Total plant food, not less than.....	per cent
Chlorine, not more than.....	per cent
Moisture, not more than.....	per cent

A statement of all the materials from which the fertilizer is made.

This form of tag shall be used for all fertilizer materials as well as for complete fertilizers.

The amendment provides no tolerances. The section amended provided that "fertilizer found upon analysis by the State Chemist materially deficient in valuable ingredients shall be subject to the penalties of the law".

\* \* \* Section 5711, Revised General Statutes. Any manufacturer or dealer who shall misrepresent the proportion of ammonia and the source thereof, phosphoric acid and potash, or other ingredients contained in such fertilizers, cotton-seed meal, castor pomace, tobacco stems, tobacco dust or tobacco meal, shall be fined five hundred dollars for the first offense and one thousand dollars for each subsequent offense.

Section 2401, Revised General Statutes. Any manufacturer or importer of, or agent for the sale of commercial fertilizers, previous to offering the same for sale in this State, shall file with the Commissioner of Agriculture annually a paper giving the name of his principal agent or agents in the State of Florida, also the name and guaranteed analysis, under oath, of the fertilizer or fertilizers offered for sale by him.

Section 5708, Revised General Statutes. Any manufacturer, importer or agent who shall refuse to give the information herein required, shall be fined five hundred dollars for each offense.

\* \* \* Section 2406, Revised General Statutes. Any person purchasing any fertilizer or fertilizing material from any manufacturer or vendor who shall upon an analysis by the State Chemist, discover that he has been defrauded, by reason of adulteration or deficiencies, of constituent elements, either in quality or quantity, in the fertilizing materials so purchased, shall recover in any action he may institute, upon proof of the fact, twice the amount paid to or demanded by the manufacturer or vendor for the fertilizer or fertilizing material so purchased.

The Florida law provides that all chemical determinations shall be made according to the methods adopted and promulgated by the A. O. A. C. The writer has been unable to find the term "available" applied to any fertilizer constituent in the methods of the A. O. A. C.



The term "available phosphoric acid" has been adopted commonly by the trade and numerous chemists, is also used in numerous laws, and is applied to the result obtained by subtracting "the citrate-insoluble from the total", which gives the water-soluble and the citrate-soluble phosphoric acid. This result has been generally termed by the trade, and is recognized by many States, as "available phosphoric acid".

The Agricultural Department of Florida has arbitrarily selected the "water-insoluble organic nitrogen insoluble in neutral permanganate" as the "inactive water-insoluble organic nitrogen" (36 and 37)<sup>1</sup>. This result is subtracted from the total nitrogen (24)<sup>2</sup> to obtain the "available nitrogen" in mixed fertilizers.

A large amount of work has been performed by various official and commercial chemists to determine chemically the availability of organic nitrogens in organic materials, so far without positive or concordant results. No method familiar to the writer for the chemical determination of "available" nitrogen in mixed fertilizers has been adopted. Nor has any study been made for available and insoluble nitrogen in mixed fertilizers.

The paper by Hartwell and Pember of the Rhode Island Experiment Station, read before the A. O. A. C.,<sup>3</sup> discusses fairly the terms "available" and "active", as follows:

The word "activity" is suitably indefinite. It, instead of "availability", should always be used when referring to the chemical methods, and should be accompanied by the name of the particular method employed.

This conclusion is certainly correct, as "availability" has not been chemically determined.

At the call of the State Chemist of South Carolina, the State Chemists of Georgia (R. E. Stallings), of Alabama (B. B. Ross), of Florida (R. E. Rose), of South Carolina (R. N. Brackett), and of North Carolina (B. W. Kilgore) met in Atlanta, November 22, 1910, and adopted the neutral permanganate as a provisional method. The Southern Agricultural Workers' Association was then in session at Atlanta, and a committee was appointed to "consider laboratory methods and to make field tests of new ammoniates" and to "report at the next meeting of this association". In 1912, the following recommendation of the referee was adopted:

1. That the modified neutral permanganate method of Street, as published in the Journal of Industrial and Engineering Chemistry, Volume 4, No. 6, page 438, be adopted.

The experience of the Florida State Laboratory and of a number of official and commercial chemists is that a uniform weight sample of

<sup>1</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 11.

<sup>2</sup> *Ibid.*, 7.

<sup>3</sup> *J. Assoc. Official Agr. Chemists*, 1923, 7: 55.

the original material should be used in the determination of the water-insoluble neutral permanganate-insoluble nitrogen, rather than a 50 mg. sample of water-insoluble nitrogen; also that more concordant results are obtained by using a one gram sample of the original material.

The problem presented is the following: "Shall the term 'available' be recognized by the A. O. A. C. as applicable to the result found by subtracting the insoluble nitrogen by the neutral permanganate method from the total nitrogen of the sample of mixed fertilizer? and Shall the sample taken for the determination of the insoluble organic nitrogen be one gram?"

It is the opinion of the writer that availability can not be definitely determined chemically; that it is not a proper term to be injected into the chemical methods of analysis of the A. O. A. C.; and that pot experiments are not conclusive as to the percentage of available nitrogen in organic materials and are of little or no value where mixed (complete) fertilizer, containing organic and inorganic nitrogenous materials, is considered.

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The preceding paper was referred by the chairman to the Committee on Definition of Terms and Interpretation of Results on Fertilizers.

## A STUDY OF AVAILABLE ORGANIC NITROGEN IN MIXED FERTILIZERS.

By GORDON HART (Department of Agriculture, Tallahassee, Fla.).

The object of this study is to improve the neutral permanganate method so that it can be applied practically to active organic nitrogen in mixed fertilizers.

As the method now stands an amount of fertilizer equivalent to 50 milligrams of water-insoluble organic nitrogen is washed onto an 11 cm. filter paper. This sample is then transferred, with 25 cc. of water for digestion, from the paper to a 300 cc. beaker. It is impossible to make this transfer without leaving some of the material on the filter. The filter should go with the sample, and sufficient permanganate should be added to accomplish this.

The size of the sample in mixed fertilizers is very important; it will vary from less than one-half gram to over ten grams if 50 milligrams of water-insoluble organic nitrogen is to be used. One chemist's results on the determination of the water-insoluble nitrogen may so differ from another's as to make a considerable difference in the size of the sample used for the neutral permanganate digestion.

Judging from the results obtained and shown in Table 1, it would seem that the best agreement can be obtained by using the same amount

of the sample irrespective of the quantity of water-insoluble nitrogen present. A study of the action, upon 12 samples of mixed fertilizers, of the digestion with the permanganate as prescribed in the present official method using varying amounts of the samples shows the limits which it is best not to exceed and indicates the size of the sample which it would be best to use.

TABLE 1.  
*Results showing the limits on the size of sample.*

NUMBER	WATER-INSOLUBLE NITROGEN	NEUTRAL PERMANGANATE INSOLUBLE NITROGEN				
	1.00 Gram Sample	0.35 Gram Sample	0.85 Gram Sample	1 Gram Sample	2 Gram Sample	3 Gram Sample
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	0.73	....	0.08	0.06	0.05	0.10
2	1.56	0.14	0.13	0.13	0.18	0.21
3	1.43	0.28	0.13	0.119	0.16	0.22
4	1.55	0.19	0.09	0.119	0.14	0.21
5	1.36	0.18	0.06	0.12	0.12	0.16
6	1.23	0.28	0.11	0.06	0.11	0.18
7	1.28	0.11	....	0.08	0.13	0.17
8	1.71	0.09	....	0.08	0.02	0.19
9	1.33	0.12	....	0.068	0.02	0.12
10	1.28	0.13	....	....	0.13	0.19
11	1.24	0.04	..	0.09	0.11	0.18
12	1.36	0.09	....	0.085	0.076	0.15

The quantity used was not carried past 3 grams, as over half of the sample showed exhausted permanganate in the filtrates, and the filtrates of the others showed the permanganate to be almost exhausted. The strength of the standard acid used was 0.5N. Thus, in the 0.35 gram sample, the error was more than doubled, and it was difficult to obtain results on the sample that checked. The figures given are the average of two determinations on the 0.35 gram sample. A blank was used in figuring all these percentages.

From the results shown a 1 or 2 gram sample would be the best to use, since less than one gram gives too much of a probable error, and three grams uses up all the permanganate.

The use of a portion of fertilizer equivalent to 50 milligrams of water-insoluble nitrogen may be all right for work on crude materials, but in mixed fertilizers the permanganate acts upon other things. It may be the filler used or the phosphoric acid may be in such a condition as to be affected.

Table 2 shows the action of the permanganate on phosphoric acid in various materials.

The results in Table 2 show that water-insoluble phosphoric acid is acted on by the neutral permanganate. From this it would seem that

results obtained on a 50 milligram sample of water-insoluble nitrogen are not correct unless the phosphoric acid is present as ammonium phosphate.

TABLE 2.  
*Action of permanganate on phosphoric acid.*

SAMPLE	WATER INSOLUBLE $P_2O_5$	PERMANGANATE INSOLUBLE $P_2O_5$	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1. Tankage. ....	12.50	11.50*	11.50†
2. Fish scrap. ....	9.00	7.70	7.80
3. Fish scrap. ....	7.00	5.75	...
4. Peruvian guano. .	8.25	7.30	7.20
5. Ground bone. . .	21.95	20.10	.
6. Mixed fertilizer. .	15.50	14.20	14.20

\*2 gram sample.

†1 gram sample.

As this work shows that in mixed fertilizers it will be valuable to make a study of the size of the sample to be used, it is suggested that parallel work on the same set of samples be carried on for the purpose of adopting a uniform size sample in mixed fertilizers. It is also suggested that a study be made of the transfer of the filter paper, together with the water-insoluble nitrogen, in the permanganate digestion.

## REPORT ON NITROGEN.

By A. L. PRINCE (Agricultural Experiment Station, New Brunswick, N. J.), *Associate Referee.*

Owing to the lateness in the year when a change was made in this refereeship, no cooperative work on nitrogen has been attempted, but plans have been formulated for the coming year.

The referee suggests that the work for next year be in accordance with a recommendation made in 1922, that a study be made of the Devarda method<sup>1</sup> as applied to the nitrates of commerce. The Moore method<sup>2</sup> for nitrates might also be tried on the same samples and the results compared. It would be well to study further the use of sodium thio-sulfate as a substitute for sodium or potassium sulfide in precipitating mercury in the Kjeldahl method<sup>3</sup>.

It is the opinion of the referee that better cooperation and work would be obtained if the details were concise and not too numerous. It is better to have one point well established by data from a large number of collaborators than to have several points undecided.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1922, 5: 451.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1920, 12: 669.

<sup>3</sup> *Assoc. Official Agr. Chemists, Methods*, 1920, 7.

The work of the collaborators for 1921 and 1922 has shown the desirability of the Devarda method when applied to pure nitrates, and it is hoped that the method will prove as accurate when applied to the commercial products. The simplicity of the Devarda method, together with the concordant results that have been obtained among collaborators in the past, lends much promise for its adoption.

To be specific, the referee proposes to submit to collaborators three different commercial samples of nitrates and have each determined in triplicate by the Devarda alloy method as tentatively written for pure nitrates. Three blanks will be run on the reagents.

Each sample is also to be run in triplicate by the Kjeldahl-Gunning method as modified by H. C. Moore.

These determinations will be repeated, the collaborators using two grams of sodium thiosulfate to precipitate the mercury instead of potassium sulfide (potassium sulfide oxidizes quite readily and also is apt to contain impurities).

It might be of interest to know that the Devarda method has been tried out successfully by the Calco Chemical Company, at Bound Brook, where many nitrate shipments are received. A. S. Eastman, under whose direction the work was done, wrote I. K. Phelps, the former referee, that the Devarda method proved to be entirely satisfactory and reliable.

No report on potash was made by the associate referee.

## THE OFFICIAL LINDO-GLADDING METHOD FOR THE DETERMINATION OF POTASH.

(With special reference to the strength of alcohol wash for the potassium-chloro-platinate precipitate.)

By R. N. BRACKETT (Clemson Agricultural College, Clemson College, S. C.).

"Some Results of the Determination of Potash by the Lindo-Gladding Method" was the title of a paper presented by H. C. Moore and R. D. Caldwell<sup>1</sup> before the Fertilizer Section of the American Chemical Society, 60th Annual Meeting, Chicago, Ill., September 6-10, 1920. The points raised by these investigators, which they deemed worthy of consideration by this association, will be made clear by the following quotations from the paper cited:

The writers found, however, that results obtained with 95 per cent alcohol were but slightly higher than those with 80 per cent alcohol when using a sample of pure potas-

<sup>1</sup> *J. Ind. Eng. Chem.*, 1920, 12: 1188.

sium chloride, but that the discrepancy was greater in case of a sample of potash salts containing chlorides and sulfates of sodium and other elements. \* \* \*

The results indicate that the presence of sodium chloride or sodium sulfate causes low results when using 80 per cent alcohol, and that when using 92 per cent alcohol the results are practically the same whether sodium salts are present or not. \* \* \*

No very complete study of the effect of various salts or the strength of the alcohol used in washing is covered by the results given above, but sufficient has been done to warrant the further careful study of this subject. The effect of other salts, such as those of calcium and magnesium, should be included. The data do seem to warrant the suggestion that the official method be changed at least to allow the use of the strong alcohol, about 95 per cent, for the first washings to remove excess platinic chloride, and the 80 per cent alcohol for final washing, if this is considered necessary; then, if there is anything present which 80 per cent alcohol should remove, and which 95 per cent alcohol will not remove, it can be done in the final washing without including the effect of sodium or other salts.

This matter was brought to the attention of the association at its 36th annual meeting, 1920, but neither the referee nor Committee A had a report on potash, according to the record.

The proceedings for the 37th annual meeting show the following recommendation by Committee A:

That the method by Moore and Caldwell which calls for the use of stronger alcohol in connection with the Lindo-Gladding method be further studied. This was recommended at the last meeting, but no samples were sent out to collaborators.

At the 38th annual meeting of the association, 1922, the associate referee, J. T. Foy, upon the suggestion of the general referee, prepared a paper that gave an account of the chief work that had been done by the association on the question of the strength of alcohol wash and other features of the Lindo-Gladding method. No samples were sent out for collaborative work, because it seemed best to the members of the association and to the general referee to find out just what had been done, it being the general impression that this point had already been exhaustively studied and that no further work was necessary, at least on the strength of alcohol wash. Committee A made the following recommendation, which was adopted by the association:

That the general referee on fertilizers for the ensuing year study the literature with regard to the use of alcohol stronger than 80 per cent for washing the potash precipitate with a view to ascertaining if collaborative investigation of the question is desirable.

In 1885, when Gladding presented the Lindo-Gladding method to this association, he said: "The labor and great care required to make an accurate potash estimation by the standard method in fertilizer analysis has led to an examination of a method proposed by Lindo<sup>1</sup>". In his adaptation of the Lindo method to fertilizers, especially mixed fertilizers, Gladding used 5 cc. of sodium chloride solution (20 grams per

<sup>1</sup> *Chem. News*, 1881, 44: 129.

liter) and washed with (pure) alcohol to get rid of the excess of platinic chloride; then after the ammonium chloride wash, finished washing with "chemically pure alcohol". This method was adopted as an alternative method in 1886, and as "the standard for the ensuing year", in 1887.

At the 5th annual convention, 1888, the committee on potash, John A. Myers and William Frear, recommended the use of the Gooch crucible (previously suggested by H. W. Wiley in 1884) and washing the precipitate with 80 per cent alcohol, completing the washing with "pure alcohol" after transferring to the Gooch, a modification proposed by the New Jersey Agricultural Station. This report was adopted by the association.

At the 8th annual convention, 1891, Winton and Frear called attention to the fact that it was apparently unnecessary to use the sodium chloride solution, and, in 1892, the addition of this reagent was omitted from the Lindo-Gladding method.

H. J. Wheeler, reporter on potash, at the 12th annual convention, 1895, recommended "that all alcohol washings be made with 80 per cent alcohol". This recommendation was adopted. From the following statements, found in the proceedings of this association, it is evident that these steps were based upon thorough investigation.

Norman Robinson, reporter on potash, in his report at the 10th annual convention, 1893, says: "As German and other authorities entitled to the highest respect have recently challenged the accuracy of the Lindo-Gladding method of potash estimation, it was recommended that the work of the association for the present year should be especially directed to an investigation of real or supposed sources of error in this official method".

A. L. Winton, reporter on potash, opens his report at the 13th annual meeting, 1896, with this statement: "The reporter on potash for the years 1894 and 1895, H. J. Wheeler, realized the importance of learning more with regard to our old methods before taking up the various new methods which had not yet been tried by the association, and accordingly confined the work carried on during the two years to a thorough investigation of the Lindo-Gladding and 'optional' methods as applied to mixed fertilizers. Since in this country the larger part of the potash which is sold to the farmers is contained in mixed fertilizers, it was desirable that our methods for the analysis of these goods be first tested. \* \* \* This work accomplished it was thought proper during the present year to carry on a similar investigation with German potash salts."

Wheeler, in the opening paragraph of his report in 1894, says: "In considering what line of work to take up, your reporter was convinced, in view of recent criticisms of one of our methods for potash determination, that a thorough test of the accuracy of present methods was de-

manded. If the methods of this association are charged with being faulty or inferior to others, it should be our immediate duty to investigate the question, looking to an improvement of present methods, the adoption of better ones, or a refutation of the charges in question. Reference is made in this connection more particularly to the statements by Breyer and Schweitzer<sup>1</sup> and to those embodied in a communication from the German Kali Syndicate, entitled 'A description and critique of various methods of potash analysis'". At the close of his two years' work as reporter, Winton being associate reporter for 1895, Wheeler, when called upon for recommendations, said: "I think there is only one recommendation that the reporters desire to make, and that is that the alcohol be made to read 80 per cent instead of strong alcohol in one, and 80 per cent in the other. The recommendation is that all alcohol washings be made with 80 per cent alcohol".

Thus in his two years' work as reporter on potash, Wheeler established the accuracy of the Lindo-Gladding method for mixed fertilizers. In this work he had the cooperation and collaboration of William P. Headden, Colorado College; W. A. Powers, Illinois Station; F. P. Veitch, Maryland College; W. L. Rossman, Michigan Station; J. P. Street, New Jersey Station; B. L. Hartwell, Rhode Island Station, K. P. McElroy, U. S. Department of Agriculture; R. deRoode, West Virginia Station; W. H. Allen, North Carolina Station, J. B. Lindsey, Massachusetts Station; W. G. Brown, U. S. Department of Agriculture; E. P. Stone, New Hampshire Station; A. L. Winton, Connecticut Station; and G. Wm. Gray, West Virginia Station. It was during the progress of this work that the 80 per cent wash throughout was proven satisfactory and adopted by this association.

A. L. Winton, to whom reference has been made, says in his 1896 report: "This work accomplished (a thorough investigation of the Lindo-Gladding and optional methods as applied to mixed fertilizers) it was thought proper during the present year to carry on a similar investigation with German potash salts. \* \* \* The following chemists took part in the study of the Lindo-Gladding and optional methods: B. B. Ross, State Chemist of Alabama; W. G. Brown, U. S. Department of Agriculture; G. W. Cavanaugh, Cornell Experiment Station; F. S. Shiver, Clemson Agricultural College Experiment Station; F. B. Bomberger, Laboratory of State Chemist, Maryland Agricultural College; C. G. Hopkins, Illinois Experiment Station; and C. H. Jones, Vermont Experiment Station.

A few quotations from Winton's report will give the results of the work and conclusions as to the accuracy of the Lindo-Gladding method:

<sup>1</sup> *J. Anal. Applied Chem.*, 1892, 6: 470.



The Lindo-Gladding method has been developed by the successive labors of Finckner, Lindo, Gladding, and members of this association. The solution in which potash is to be determined is evaporated with platinum solution without previous separation of bases or sulphuric acid, the sulphates which contaminate the potassium platinum-chlorid being subsequently removed by ammonium chlorid solution. The method is rapid, and as will be seen later, *remarkably accurate*. \* \* \*

Notwithstanding the criticisms of Breyer and Schweitzer, the Stassfurt chemists, Vogel and Haefcke, *the results of eight chemists working independently of each other in different laboratories and with different reagents, agree in establishing beyond a doubt, the remarkable accuracy of the Lindo-Gladding Method.*

*An experienced analyst who follows strictly the instructions and uses a Gooch crucible should find it rapid, economical, and accurate.* \* \* \*

If ammonium chlorid solution be poured through the double salt contained on an ordinary filter paper double decomposition may take place, the impurities may not be washed out thoroughly and the difficulty in removing the ammonium chlorid with alcohol may be encountered. \* \* \* Renner first pointed out that this reaction takes place, but his results show that the change is very gradual. \* \* \* A saturated solution of ammonium chlorid at 22° C., when in contact with *finely divided* potassium platinumchlorid for one hour, decomposed but 0.27 per cent of the latter.

In his report as referee at the 14th annual convention, 1897, Winton, with C. H. Jones as associate referee, stated that the subjects investigated (so far as concerned the Lindo-Gladding method) were the determination of potash (in salts) by the Lindo-Gladding method; evaporating directly with platinum solution, without previous removal of lime; and the quantities of platinum solution necessary for the determination in German potash salts. In his comments the referee says: "The results for the past two years, both on the mixtures of pure potassium sulphate with kainit 'impurities' and on commercial kainit, demonstrate that the direct evaporation process is fully as reliable as the official method. As it is in addition much shorter, and much more easily carried out, there is abundant reason for returning to this, the original method, which, if the two methods had been thoroughly investigated six years ago, would probably never have been abandoned." As to the amount of platinum solution, he says: "It appears that a saving of platinum solution can be readily effected without interfering with the accuracy of the method". The suggested method for kainit, direct evaporation, was adopted by the association on the recommendation of the committee on potash methods.

At the 15th annual convention, 1898, C. H. Jones, referee, with B. B. Ross, associate referee, reported as a result of the year's work the applicability of the Lindo-Gladding method to the determination of potash in wood ashes and cotton-hull ashes. They also suggested that Gooch crucibles be used for filtering the potassium platinumchlorid precipitate, when the Lindo-Gladding method is used. This suggestion led to some discussion, Ross calling attention to his experience with asbestos and Gooch filters, to the effect that the asbestos is attacked slightly by the

ammonium chloride solution. C. H. Jones replied that previous treatment with hydrochloric acid prevented this, but that there might be some mechanical loss of fibers of asbestos carried through. On recommendation of the committee on potash methods, the Lindo-Gladding method was adopted by the association for ashes, as recommended by the referee, with his proviso of special attention to the words "the precipitate should be perfectly soluble in water".

In connection with his report as referee on potash at the sixteenth annual convention, 1899, San Francisco, Calif., B. B. Ross sent with his report "a short résumé of the work on this subject performed by the association since its inception fifteen years ago", this paper having been prepared at the suggestion of the secretary of the association, H. W. Wiley, whose most valuable historical sketch of this association also appears in the proceedings of this convention. The following is a brief abstract of Ross's paper:

A convention of agricultural chemists had been held at Washington, D. C., July 28, 1880, and had adopted the following method for potash: "Solution in water, removal of sulphates, phosphates, and magnesia by barium hydrate, clearing with oxalate or carbonate of ammonia and precipitating with platinum chloride", which had the merit of brevity and allows considerable latitude for the individual analyst (comment of Ross).

This association was organized at the Philadelphia meeting September 1884, and methods for phosphoric acid and potash were adopted, the latter being much like the optional method, but differing in that hydrochloric acid was used along with water in solution of potash, no oxalic acid or ammonium oxalate was used in removing lime, two ammonium carbonate precipitations were used, and also one more filtration, evaporation, and ignition. At this convention, H. W. Wiley was appointed as chairman of a committee on potash.

At the second annual convention of this association at Washington, September, 1885, Wiley (who was associated with W. J. Gascoyne and Clifford Richardson as a committee on potash) made a report on potash methods characterized by his usual thoroughness, and also referred to the fact that little progress had been made toward unification of methods of analysis in the different countries. In this connection the following quotation from Ross's paper is interesting: "As early as 1875, steps had been taken by the British Association for the Advancement of Science looking toward the securing of uniformity in methods of analysis of fertilizing materials, and a commission appointed for the purpose endeavored to secure from the leading chemists engaged in commercial analysis a statement as to the methods employed in their laboratories for potash and phosphoric acid work. They were not altogether successful, however, in their request for information of this character, as one prominent firm of commercial chemists declined to give the information desired, 'as we do not think ourselves called upon to publish our methods of analysis, which we have perfected after long and careful investigation, for the benefit of those who have not taken this trouble'. Fortunately chemists of this character are the exception rather than the rule, and the committee referred to, as well as the Society of Public Analysts, have been able to do much toward the harmonizing of diverse methods of analysis in spite of opposition from such sources. As the result of the work of this committee, the process of Wallace, Tatlock, and Clark

was brought into notice<sup>1</sup>, the prominent feature of this method being the washing of the double chloride of potassium and platinum with a solution of platinum chloride".

At this same 1885 convention, T. S. Gladding presented his now famous paper, giving the results of tests of the original Lindo method, and, most important, the modification of this method so as to adapt it to the determination of potash in fertilizer materials and mixtures. The Lindo-Gladding method was published in the proceedings of this meeting. Another action of importance at this meeting was the omission of hydrochloric acid in making the potash solution, as a result of facts and suggestions contained in Wiley's report referred to above.

At the annual convention in 1886, the third, the Lindo-Gladding method was adopted as an alternative method, while at the 4th annual convention, 1887, the Lindo-Gladding took precedence over the then official method, and the latter was relegated to the position of alternative or optional.

At the annual convention in 1888, the fifth, on the recommendation of E. B. Vorhees, New Jersey, the Lindo-Gladding method was modified to the extent of adding ammonium oxalate in addition to ammonia to remove lime.

No changes were made in the Lindo-Gladding method during 1889 and 1890, but at the 8th annual convention, 1891, a change was adopted to add ammonia before ammonium oxalate, and to add the latter to the hot solution. At this meeting also A. L. Winton, Connecticut, presented a paper in which was set forth the desirability of omitting the use of sodium chloride. This suggestion of Winton was tested very thoroughly by G. F. Payne, reporter on potash for 1892, and the use of sodium chloride was discontinued by the association at its 9th convention in that year. Ross states that while Gladding had proposed the use of sodium chloride in the Lindo-Gladding method, its use in determining potash in the presence of sulphates had been proposed by Wallace, Tatlock, and Clark in 1875.

At the 1891 meeting a change was made in the determination of potash in kainit, remarkable in that it was made without request by the reporter and without any previous investigation as to its desirability, namely, to require the use of ammonia and ammonium oxalate to precipitate lime. At the annual meeting in 1897, on the recommendation of Winton, the referee on potash, the association returned to the original method, omitting the use of ammonia and ammonium oxalate in the Lindo-Gladding method for potash in potash salts—German salts.

Ross refers to the excellent work of Wheeler (1894 and 1895) and that of Winton (1896), in the following terms: "During the past few years Messrs. Wheeler and Winton, as referees on potash, have tested the accuracy of the Lindo-Gladding and optional methods quite thoroughly by the employment of chemically pure potash salts, mixed with varying proportions of the impurities commonly met with in crude potash salts. Cooperation on the part of German chemists was also secured to a limited extent in testing the comparative merits of the Lindo-Gladding and Stassfurt methods, and the Stassfurt method has also been given an official trial by this association, with results not at all disadvantageous to our present official method".

Ross reported that the work for the year (1899) was confined to materials containing at least a part of their potash in organic forms. He did not recommend any change in methods for potash, but suggested that the use of 1:1 sulphuric acid be allowed as optional for saturating mixed fertilizers preparatory to ignition. Ross also called attention to a comparison of the Gooch crucible and tared paper for weighing potassium platinum precipitate; while the results were too few to draw a final conclusion, they indicate that "it is possible to secure quite satisfactory results by employment of the latter process of filtration".

<sup>1</sup> *Chem. News*, 1875, 32: 201.

Perhaps the most important problem worked on by L. S. Munson, referee, and C. L. Hare, associate referee, and reported at the 17th annual meeting, 1900, was the determination of the potash in mixtures of acid phosphate and pure potassium chloride. In a mixture in which the theory called for 6.35 per cent water-soluble potash, the average found was 6.12, while a 3.23 mixture gave on analysis an average of 3.07 per cent water-soluble potash. Huston pointed out that higher results were obtained by passing steam through when preparing the solution, thus diluting rather than concentrating the solution.

At the 18th annual convention, 1901, C. L. Hare, referee on potash, reported that the work of the year, in the absence of recommendations by Committee A at the previous meeting, had been "a continuation of the previous year's inquiries suggested by F. B. Carpenter, concerning the probable failure of the Lindo-Gladding method to obtain from mixtures of acid phosphate and potash salts the theoretical amount of potash added", and also "the use of ammonium chloride in securing all the potash present in such mixtures". He reported that the ammonium chloride seemed to be of no practical value in this connection. The referee also included in his work the Ross "milk of lime" method (applicable only to fertilizers containing organic matter and mixtures of acid phosphate and potash salts). It is directed to add the milk of lime after making the solution of potash according to the official method and while the solution is still hot; then boil, cool, make up, take aliquot, acidify with hydrochloric acid, and evaporate with platinum solution. The referee recommended a continuation of study on the causes of the low results obtained by the official method, and also of the milk of lime method. It is interesting to note that the mixture of acid phosphate and potassium chloride which contained 3.35 per cent of potash gave by the Lindo-Gladding an average of 3.12, by milk of lime method 3.15, and by the use of ammonium chloride 3.19 per cent of potash. The two recommendations made by the referee were also recommended by Committee A and adopted by the association.

At the annual convention, H. B. McDonnell, referee on potash for 1902, with H. D. Haskins, associate referee, reported on causes of low results obtained by the official method, as well as on the milk of lime method and the determination of moisture in potassium salts. The investigation of the first problem involved the use of sulfate of potash, kainit, and mixtures of these with acid phosphate alone, and with blood and fish meal. In addition to the Lindo-Gladding and milk of lime methods, the barium chloride-ammonium carbonate method of McDonnell was also tried. The average results by the different methods agreed very closely, but all fell short by from 0.2 to 0.4 per cent, except in two cases where the milk of lime gave high results. The referee comments: "The results further emphasize the fact that our methods fail

to recover all of the potash from mixed fertilizers, especially those containing acid phosphate". The referee recommended further experiments for the purpose of securing a method that will dissolve all of the potash in mixed fertilizers, and that some latitude for the judgment of the analyst be allowed in regard to the amount of substance taken. This recommendation was endorsed by Committee A and adopted by the association.

F. B. Carpenter, referee, with M. G. Donk as associate referee, reported at the 20th annual convention, 1903, a continuation of the investigation of low results by the official method, using mixtures of pure potassium chloride and acid phosphate. The results were about as usual, and did not warrant any change in the method. The referee suggested the use of a little hydrochloric acid to liberate occluded potash and neutralization with sodium hydrate instead of ammonia to prevent the occlusion of potash, which is usually found when using ammonia and ammonium oxalate. This introduces salt as in the original Lindo-Gladding method. Results promising. Committee A recommended that the question of further trial of the modification requiring a slightly acid solution and neutralization by soda be left to the discretion of the referee. This recommendation was adopted.

F. B. Carpenter, referee, with G. S. Fraps as associate referee, reported at the 21st annual convention, 1904, a continuation of the investigation of the preceding year—the cause of low results by the official potash methods, especially the Lindo-Gladding, using pure potassium chloride mixed with acid phosphate and also a sample of these materials mixed with animal tankage. The modified method with acid, etc., gave results very close to theory, while the official method gave the usual low results. The referee made the following recommendation:

That the directions for making the solution in mixed fertilizers given under the determination of potash methods of analyses<sup>1</sup> be made to read as follows: Boil 10 grams of the sample with 300 cc. of water plus 5 cc. of hydrochloric acid for thirty minutes. Add a few drops of phenolphthalein and carefully neutralize with sodium hydrate free from potash, avoiding a large excess. Add sufficient powdered ammonium oxalate to precipitate all the lime present, cool, dilute to 500 cc., mix and pass through dry filter. The method for the solution of potash is to remain as at present.

This recommendation was submitted, recommended by Committee A, but action was deferred by the association until 1905, on account of changes involved in the official method.

At the annual convention for 1905, G. S. Fraps, referee on potash, stated that "the work on potash in mixed fertilizers has been confined to (1) a comparison of the official and modified methods on mixtures of known composition and (2) the determination of the amount of potash extracted from insoluble potash compounds by the modified method".

<sup>1</sup> U. S. Dept. Agr. Bur. Chem. Bull. 46: 21.

The modified method is given as follows: "Boil 2 grams of the sample 30 minutes with 300 cc. of water plus 5 cc. of concentrated hydrochloric acid. Add a few drops of phenolphthalein and carefully neutralize with caustic soda, free from potash, avoiding a large excess. (The referee uses a 10 per cent solution.) Precipitate the lime with ammonium oxalate and complete the determination as by the official method. Five cc. of platinum solution of such strength that 1 cc. precipitates 1 per cent of potassium oxide should be sufficient to precipitate all the potash, as it is unnecessary to use sufficient platinum to combine with all the soda". In commenting on the results of the work, Fraps stated that the modified method gives accurate results, which are nearer the theoretical figures than those given by the official method, as was also shown by the previous referee; that taking the maximum and minimum of all results, the difference is less for the modified than for the official method—that is, the determinations come closer together. It must be concluded that the modified method gives results more nearly correct than does the official method. Fraps made experiments to ascertain how much, if any, potash would be removed from insoluble silicates that might be used as fillers in mixed fertilizers in case the modified method were used, and found that only small amounts (from 0.08–0.30 per cent) were dissolved from these minerals by the modified method, except from muscovite, and even in that case only 0.41 per cent more was obtained than by the official method. He states that if 500 pounds of any of these materials were used for a filler in fertilizers, the maximum increase in the percentage of potash would be 0.08 per cent. Fraps finally says that he is inclined to think that the modified method does not open the way for the more extended use of potash-bearing silicates as a filler, as the amount of potash that could be added is insignificant. The referee then called attention to the large number of States requiring the guarantee of water-soluble potash, and expressed a desire to have the association discuss the point as to whether, under the existing laws, a method requiring the addition of 5 cc. of hydrochloric acid in 500 cc. of water for solution can be used. He stated further that inasmuch as the modified method appeared to be accurate and more nearly gave credit for all the potash placed in a mixed fertilizer and did not seem to open the way to the use of silicates bearing potash (as fillers), he was willing to indorse the following recommendation of the previous referee, which had gone over this year under the rule: "That the modified method be adopted as the official method". He added, however, that he hesitated to give his unqualified endorsement to the recommendation owing to the fact that the association might think it inadvisable to adopt the modified method, when 27 States had laws requiring water-soluble guarantees. The following is taken from the report of Committee A: "(3) (The association is asked to consider carefully the adoption as

official of the following two methods coming over from the preceding year for final consideration, the referee for 1905 not giving these changes an unqualified endorsement): 1st—That the directions for making the solution in mixed fertilizers given under the determination of potash in Bull. 46, page 21, be made to read as follows:

“Boil 10 grams of the sample with 300 cc. of water plus 5 cc. of hydrochloric acid for thirty minutes. Add a few drops of phenolphthalein and carefully neutralize with sodium hydrate free from potash, avoiding a large excess. Add sufficient powdered ammonium oxalate to precipitate all the lime present, cool, dilute to 500 cc., mix, and pass through a dry filter”.

This recommendation received only a qualified indorsement by the referee for 1905 and after some discussion by Messrs. Frear, Carpenter, Hartwell, and Wiley, the vote was taken, in which only chemists in charge of fertilizer control were qualified to participate, the vote resulting in the loss of the motion. It seemed to be the opinion of the majority that the time was not ripe for the adoption of a change, although some modification of the method might be desirable.

From the 23rd to the 26th, inclusive, annual conventions, that is during the years 1906 to 1909, inclusive, no work on potash that concerned the Lindo-Gladding method seems to have been done.

E. L. Baker, referee on potash, reporting at the 27th annual convention, stated that to the study of Drushel's volumetric cobalti-nitrite method in comparison with the official method, there was added a test of the modification of the official method of making up the potash solution, as described by Breckenridge<sup>1</sup>. This consisted of washing a weighed amount (2 grams) of fertilizer on a filter paper and determining the potash in the filtrate as it is used at the present time. Thirty-two samples were examined in this way, and only four samples showed less potash by the modified than by the official method, the greatest loss being 0.1 per cent. One sample showed no difference, and 27 samples gave larger amounts of potash by the modified method, the increase ranging from 0.05 to 0.54 per cent. Baker, therefore, recommended that a further trial be made of the modified official method by washing a weighed amount of the sample through filter paper with hot water and determining potash in the filtrate. Committee A recommended that a further trial of this modification be made, and the recommendation was adopted by the association.

At the 28th annual convention, Baker, reappointed referee on potash, gave the results of the further trial of the Breckenridge modified method and recommended that changes as published<sup>2</sup> be made in the methods for making solutions for potash. Committee A approved the recom-

<sup>1</sup> *J. Ind. Eng. Chem.*, 1909, 1: 409, 804.

<sup>2</sup> *U. S. Dept. Agr. Bur. Chem. Bull.* 152: 41.

mentation of the referee and referred the matter to the association for final adoption in 1912.

At the 29th, 1912, annual convention, H. B. McDonnell, referee on potash, recommended the adoption of the following Breckenridge modification, which was approved by Committee A and adopted by the association as official:

Weigh 2.5 grams of the sample upon a 12.5 cm. filter paper and wash with successive small portions of boiling water into a 250 cc. graduated flask to a volume of about 200 cc. In the case of mixed fertilizers add 2 cc. of concentrated hydrochloric acid, heat to boiling, and add to the hot solution a slight excess of ammonium hydroxide and then sufficient ammonium oxalate to precipitate all lime present; cool, dilute to 250 cc.; mix; and pass through a dry filter.

At the 30th annual convention, 1913, H. B. McDonnell, referee on potash, recommended further study on (1) denatured alcohol wash for the platinum precipitate, which he said had been referred to at the previous meeting; and (2) whether or not it is necessary to add hydrochloric acid to the filtrate and boil in the Breckenridge modified official method. These recommendations were approved by Committee A.

T. D. Jarrell served as referee on potash from 1914 to 1917, inclusive, and the two recommendations made by H. B. McDonnell in 1913 were investigated, with the result that in 1915 Jarrell recommended that the use of denatured alcohol be allowed as an alternative with 80 per cent alcohol. This was approved by Committee A and adopted by the association. Jarrell specified the formulas for the denatured alcohol. He also reported at this meeting that the use of hydrochloric acid in the Breckenridge modification had been found unnecessary, but Committee A recommended further work on this point.

Further work was done on the use of hydrochloric acid during the next two years, and at the 33rd and 34th (1916 and 1917) conventions Jarrell repeated his recommendation to discontinue the unnecessary use of hydrochloric acid. Committee A approved and the association adopted his recommendation in 1917.

There was no meeting of the association in 1918. Nothing of importance in reference to the Lindo-Gladding method was recorded at the 35th convention, 1919, or at the 36th, 1920.

At the 37th annual convention, 1921, Committee A made the following recommendations on potash, which were approved by the association: "(1) That the method by Moore and Caldwell<sup>1</sup> which calls for the use of stronger alcohol in connection with the Lindo-Gladding method be further studied. This was recommended at the last meeting, but no samples were sent out to collaborators". At this convention William Hazen of the Bureau of Soils, U. S. Department of Agriculture, read a

<sup>1</sup> *J. Ind. Eng. Chem.*, 1920, 12: 1188.



very interesting paper on the determination of small amounts of potash by the Lindo-Gladding method, at the close of which he says:

"In the determination of potash 90 per cent alcohol gives better results than the 80 per cent solution, and when *working with small amounts of potash and high accuracy is desired*, it is advisable to use the stronger alcohol, *both before and after the ammonium chloride treatment*. However, it takes a longer time to wash out ammonium chloride salts with the 90 per cent solution. Furthermore, in ordinary fertilizer work the samples generally contain relatively high amounts of potash, in which case the percentage error arising from the use of 80 per cent alcohol will not be very serious. Therefore, in ordinary work the best procedure would be to use 90 per cent alcohol in the initial and 80 per cent in the final treatment".

## OBSERVATIONS ON THE ANALYSIS OF DOUBLE SUPERPHOSPHATE.

By E. L. LARISON (Anaconda Copper Mining Co., Anaconda, Mont.).

During the past two or three years there has been a notable increase in the manufacture and use of double superphosphates. By double superphosphate is here meant a material made by mixing finely ground phosphate rock with phosphoric acid containing about 45 per cent phosphoric acid. The mixture which contains about 20 per cent moisture is usually artificially dried to about 3 or 4 per cent moisture and then contains 45 to 48 per cent available phosphoric acid.

Results obtained in the analysis of such materials by the method of the Association of Official Agricultural Chemists have been far from satisfactory. It is indeed the exception rather than the rule to find two chemists not in the same laboratory reporting closely agreeing results; and this applies to chemists of the highest standing.

This situation, no doubt, arises largely from the fact of the high concentration of the material. When the present methods of this association were developed the acidulated phosphatic materials to be assayed were almost entirely of grades not over 16 or 17 per cent phosphoric acid. Reasonable agreement could be obtained between chemists by the official methods, but when the spread between results is multiplied by 2.5 or 3 the differences become serious.

In order to give some idea of the discrepancies that commonly occur in the analysis of double superphosphate the following example may be cited:

A carload of the material was sold on analysis. The assays of the seller and the buyer did not agree. Portions of the sample were sent to two commercial laboratories of high reputation for umpire. The results obtained are shown in Table 1.

TABLE 1.  
*Results obtained by different analysts.*

	TOTAL $P_2O_5$	INSOLUBLE $P_2O_5$	AVAILABLE $P_2O_5$	MOISTURE
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Seller . . . .	48.60	1.78	46.82	4.15
Buyer . . . .	47.94	2.26	45.68	6.00
Umpire 1 . . .	47.42	2.18	45.24	4.93
Umpire 2 . . .	48.26	1.56	46.70	4.60

Portions of another sample of similar material were sent to 33 different chemists. The results ranged as shown in Table 2.

TABLE 2.  
*Range in results obtained by 33 analysts.*

	TOTAL $P_2O_5$	INSOLUBLE $P_2O_5$	AVAILABLE $P_2O_5$	MOISTURE
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
High . . . .	49.58	3.38	46.52	5.20
Low . . . .	47.77	2.74	44.93	2.75
Average . . .	48.74	3.05	45.68	4.10
Range . . . .	1.81	0.64	1.59	2.45

The condition disclosed by such results, which are typical, certainly deserves the attention of the chemists of the fertilizer industry. The writer of this paper has had extensive correspondence and many interviews with State chemists, factory chemists, and commercial laboratories in an endeavor to discover the reasons for these discrepancies. While the work is not complete, some interesting things have been learned, and it is hoped that the presentation of them here may, in some measure, start to clear up the situation.

It may be well to state that no departures from the existing method are going to be proposed. Some causes for the frequent disagreement have been discovered. These resolve themselves into departures from the specifications of the official method that may appear trivial but are not, and the lack of definite directions in some parts of the official method as it is now written. It is thought that some amplification of these directions is required.

The writer has gained the impression that the chemists in this industry regard the official gravimetric method as that most reliable and proper for use in important work. This seems to be particularly true when applied to the analysis of these unusually high percentage materials. Wiley<sup>1</sup> says of the volumetric method:

<sup>1</sup> Principles and Practice of Agricultural Analysis, 1908, Vol. 2.

Page 155.—The strength of the (standard KOH) solution can not be safely assumed from the weight and purity of the material, but is to be ascertained by comparison with a solution of a phosphate of known composition.

Page 157.—The method works far better with small percentages of phosphoric acid. Where the average of the results by the official (gravimetric) methods gave 12.25 per cent, the volumetric process gave 11.90 per cent, whereas in the determination of a smaller percentage the results were 2.72 and 2.73 per cent, respectively.

This paper is concerned entirely, therefore, with the determination of phosphoric acid by the official gravimetric method and with the general matters of preparation of sample, determination of moisture, and washing out of water-soluble phosphoric acid.

#### PREPARATION OF SAMPLE.

The official directions for preparation of sample are clear and definite. One is told to reduce the material as rapidly as possible to such fineness that it will pass a sieve having circular holes 1 mm. in diameter, and to weigh out portions for the various analytical operations following, from the material so prepared.

It has been found on several occasions that chemists to whom samples of double superphosphates have been submitted for analysis have not been content with the degree of fineness specified by the association, and in consequence have reground the material to a much finer condition. At first glance this appears a harmless thing to do, but as a matter of fact such action may lead to serious changes in the constitution of the material. First, exposure to the atmosphere and to the heat generated in a fine grinding operation often changes the moisture content appreciably; second, double superphosphate always contains some free phosphoric acid, and when it is rubbed vigorously between grinding surfaces a portion of the material sticks to these surfaces. The portion that sticks is gummy, hard to scrape off, and very difficult to reduce to a powder. It is not, moreover, of the same composition as the portion which more easily passes through the grinding without sticking, but contains more phosphoric acid than the latter. If this sticky portion is not carefully removed from the grinding surfaces and incorporated uniformly with the remainder of the sample, low results are obtained.

This may sound like a remote and unlikely cause for incorrect results, but it is not a theory. On more than one occasion the writer has submitted samples for umpire, and when discordant figures were returned has ascertained that the samples were reground. Upon requesting repeat assays on the material without regrinding, good checks have resulted.

The point of this part of the discussion is simply to urge strict adherence to the specifications clearly laid down. Whether they are the best that could be made or not is beside the point. To get agreeing results on this high analysis material uniformity of detail is absolutely essential.

## MOISTURE.

The official directions for the determination of moisture are clear and precise, and yet surprising variations in moisture figures are common. To refer back to the figures quoted on the sample sent to 33 different chemists, Table 2, it is to be noted that there was a range of 2.45 per cent in the results reported.

It is probable that the chief causes of these variations lie in improper exposure of the samples to the atmosphere before or during the determination, and in failure to adhere strictly to the direction to "heat in a water oven at the temperature of boiling water".

A regrinding operation would obviously be a fertile cause of loss or gain of moisture.

## DETERMINATION OF TOTAL PHOSPHORIC ACID.

In finding the percentage of available phosphoric acid in double superphosphate the chief disagreement usually lies in the figures for total, rather than in insoluble phosphoric acid. There may be several causes for these differences in total, but one in particular has been found which the writer feels is highly important and upon which action by this association is deserved.

This is in the point of the condition of the solution to which magnesia mixture is added for the precipitation of ammonium magnesium phosphate. The official method directs the chemist to dissolve his washed precipitate of ammonium phospho-molybdate in ammonia and hot water and to then nearly neutralize with hydrochloric acid, cool, and add magnesia mixture in a certain fashion. It is in the fact that the term "nearly neutralize with hydrochloric acid" is indefinite that the trouble lies. The chemist can "nearly neutralize" and leave his solution ammoniacal, or he can "nearly neutralize" and leave his solution acid, or he can exactly neutralize. To show in figures the variations caused by different procedure at this point the following experiments were carried out.

1. Five samples were treated in the usual way up to the point of addition of hydrochloric acid. The solutions were cooled and hydrochloric acid was added until the solutions were neutral to litmus paper; then magnesia mixture was added, and the determinations were finished as usual.

2. Portions of the same five samples were treated in the usual way and brought to the neutral point as in 1; then to each was added 1 cc. of 1.18 sp. gr. hydrochloric acid and the precipitate thrown down with magnesia and finished as usual.

3. Portions of the same five samples were treated in the usual way and brought to the neutral point, as in 1; then to each was added a

quantity of ammonia equivalent to 1 cc. of 1.18 sp. gr. hydrochloric acid and the precipitate thrown down with magnesia and finished in the usual way.

The results are shown in Table 3.

TABLE 3.  
*Variations in three samples prepared by different methods.*

	NEUTRAL	ACID	AMMONIACAL
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	47.17	47.91	46.60
2	46.65	47.60	46.30
3	45.70	47.00	45.50
4	47.40	48.50	47.10
5	46.70	47.50	46.20

Average difference between ammoniacal and neutral..... 0.38

Average difference between neutral and acid..... 0.98

Average difference between ammoniacal and acid..... 1.36

Two chemists may easily vary as to the limits of acidity or alkalinity covered by this experiment, and each consider that he has "nearly neutralized".

With this data in view it seems highly desirable and indeed very necessary that a more definite specification be substituted for the term "nearly neutralize". A point at which the solution is neutral to litmus can be very closely reached in a cold solution. The chemist can precipitate in this neutral solution or he can, once he has established the neutral condition, make his solution acid or alkaline by addition of measured amounts of hydrochloric acid or ammonium hydroxide.

If one turns to the literature of analytical chemistry for a decision as to whether his magnesia mixture should be added to an acid solution or an ammoniacal solution, he finds that writers upon this subject almost without exception direct that the phosphate solution shall be acid. Several references may be quoted.

*Neubauer*.—(Translated and abstracted by K. P. McElroy for American Chemical Society<sup>1</sup>.) Three sets of conditions under which magnesium ammonium phosphate can be obtained, are given as follows:

(1) "The precipitate is formed in neutral or ammoniacal solution containing no excess of magnesium salt. The result of this is that the precipitate contains less than the normal amount of magnesia, and phosphoric acid is volatilized on ignition. Therefore, weights come out too low.

(2) "The precipitate is formed in the presence of an excess of magnesium salt, but during its formation ammonia is not present in excess. As a result the precipitate possesses the normal constitution and the weights obtained are correct.

(3) "The precipitate is formed in the presence of an excess of both ammonia and magnesium salts. The result is that the precipitate contains an excess of magnesia and the weights afforded are consequently too high."

<sup>1</sup> *J. Am. Chem. Soc.*, 1894, 16: 289.

*Hillebrand*<sup>1</sup>.—Page 179—"Hydrochloric acid is added to the ammoniacal filtrate until the yellow precipitate begins to reappear and does not redissolve quickly, and then a slight excess of magnesia mixture. Ammonia is now added slowly with continuous stirring until the precipitation of magnesium ammonium phosphate has been largely accomplished."

On page 148 in describing the determination of magnesium—"From their labors (Neubauer, Gooch, Austin) it would seem clear that the common way of adding the phosphate precipitant to the ammoniacal solution of the magnesium salt is not calculated to produce a precipitate of normal composition. The precipitant should be added to the acid solution of the magnesium, and ammonia should then be added in slight excess. The precipitate as ordinarily formed contains an excess of phosphorus".

*Treadwell*<sup>2</sup>.—Quoting Schmitz, Treadwell says the yellow precipitate "after standing ten minutes is filtered off and dissolved in warm 2.5% ammonia, after which hydrochloric acid is added until the yellow precipitate produced dissolves only slowly on being mixed with the solution. Now, according to Schmitz, an excess of an acid solution of 'magnesia mixture' is added, and the solution heated to boiling. A few drops of phenolphthalein are added, and an approximately 2.5 per cent ammonia solution introduced as quickly as possible from a burette, while stirring the solution, until the liquid becomes slightly red in color".

*Olsen*<sup>3</sup>.—"Neutralize the solution with strong hydrochloric acid, and if the yellow phosphomolybdate begins to precipitate, add ammonia until dissolved. A white flocculent precipitate insoluble in ammonia is probably silica, and should be filtered off. The solution is again rendered slightly acid with hydrochloric acid and enough magnesia mixture added to precipitate the phosphoric acid present \* \* \*. The solution is neutralized by adding ammonia while stirring constantly."

*Gooch*<sup>4</sup>.—"The use of strongly ammoniacal solutions induces the formation of trimagnesian phosphate \* \* \*. The constitution of the precipitate is very nearly ideal when the boiling solution of the phosphate containing a moderate excess of magnesium salt, and not more than 5 to 10% of  $\text{NH}_4\text{Cl}$  is made ammoniacal very gently."

In view of the obvious importance of this point, and the opinions of the authorities cited, the writer wishes to respectfully suggest to this association that for the term "nearly neutralize" there be substituted the direction to "neutralize the cooled solution with hydrochloric acid using litmus as an indicator, and to then add 1 cc. of 1.18 sp. gr. hydrochloric acid". Such a revision would enable the chemist to work to a definite condition and one which he could always reproduce.

#### WATER-SOLUBLE PHOSPHORIC ACID.

While this is a determination not often required in the United States, it is of some importance in itself and of great importance in the determination of citrate insoluble following and dependent upon it.

The directions are certainly plain enough, and the probable reason for failure to get good results is that they are not meticulously followed. Slow and painstaking application of the full amount of water specified is necessary.

<sup>1</sup> U. S. Geol. Survey Bull. 700.

<sup>2</sup> Analytical Chemistry, 1919, Vol. 2, 438.

<sup>3</sup> Quantitative Chemical Analysis, 1908, 120.

<sup>4</sup> Quantitative Chemical Analysis, 1916, 82.

If the chemist fails to dissolve out all of the water-soluble phosphoric acid he apparently puts an undue load upon the specified volume of neutral ammonium citrate used to digest the residue, and the citrate then fails to dissolve all the phosphoric acid that it should. This, of course, results in too high figures for the citrate insoluble.

## DETERMINATIONS OF PHOSPHORUS.

By J. B. MUDGE, JR. (Fleischmann Laboratory, New York, N. Y.).

In the official methods for the determination of phosphoric acid<sup>1</sup> in Chapter II, "Inorganic Plant Constituents", it seems wise to call attention to the fact that the directions are scarcely explicit enough, and that metaphorically speaking an open switch has been left without a red light on it as a danger signal.

In the determination of phosphoric acid in flour and in bread from an aliquot of the ash, certain difficulties present themselves in attempting to determine from the method as given exactly what the procedure should be.

These substances would not be considered rich in silica, alkalis, or phosphates, and one is left to devise a suitable method for preparation of the solution from the ash. In following the method provided under 11, "Inorganic Plant Constituents", there is nothing to prevent one from following the method provided in the chapter on "Fertilizers", Sec. 5 (a) which reads: "Ignite and dissolve in hydrochloric acid", since the directions for the preparation of the solution given under "Fertilizers", Sec. 8, volumetric method, refer to Sec. 5 in the same chapter and Sec. 5 (a) is the only one that anticipates that the determination is to be made upon an aliquot of the ash.

In making phosphoric acid determinations on samples of wheat flour according to Chapter I, Sec. 9 (a), volumetric method, it was observed the precipitates were about one half of what is considered normal. This observation was verified by the low percentages obtained.

The solution was prepared by dissolving the flour ash in the hydrochloric acid.

In this work on flour ash the filtrates from the phosphoric acid determination were carefully tested for further precipitation of ammonium phosphomolybdate. After reheating and standing 24 hours a very slight precipitate formed.

As the low results indicated an error in the procedure, the following changes were made: Two cc. of concentrated hydrochloric acid were added to an aliquot of the original solution and evaporated to dryness.

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<sup>1</sup>Assoc. Official Agr. Chemists, *Methods*, 1920, 18.

The residue was brought into solution. Precipitation of phosphoric acid was then made as before.

The results obtained in this case were much higher than before and correspond to normal percentages. This difference in results on flour ash suggested the value of work along this line embracing other material than flour.

For this work two samples of dried yeast were selected because of their high phosphoric acid content as compared with flour. Five determinations were made on each sample in order to obtain an accurate average. In the following tables data are given showing the percentages of ash and corresponding percentages of phosphoric acid in the samples of flour and yeast. The ash determinations were made at 550° C. except in the case of dried yeast No. II, which had to be burned at 450° C. because of fusing of ash at higher temperature.

TABLE 1.

*Ash and phosphoric acid in two samples of flour.*

SAMPLE NO. 100		SAMPLE NO. 101	
Ash	Phosphoric Acid	Ash	Phosphoric Acid
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0.39500	0.0556	0.68500	0.0618
0.37250	0.0556	0.68750	0.0649
0.39125	0.0464	0.68500	0.0618
0.40120	0.0309	0.69500	0.0773
0.39895	0.0371	0.68250	0.0803
Avg. 0.39176	0.0451	0.6871	0.0692

TABLE 2.

*Ash and phosphoric acid in two samples of dried yeast.*

SAMPLE I		SAMPLE II	
Ash	Phosphoric Acid	Ash	Phosphoric Acid
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
10.0630	2.1630	6.50625	1.5450
10.0000	2.1470	6.53250	1.6680
10.0262	2.1470	6.52700	1.8690
10.1125	2.1780	6.52500	1.8850
10.0460	2.1470	6.51750	1.5140
Avg. 10.0495	2.1560	6.52165	1.6960

In this and succeeding work the aliquots used for flour were equivalent to 1 gram original substance and for yeast 0.2 gram original substance.

The filtrates from phosphoric acid determinations given in Tables 1



and 2 were tested to see if the precipitations had been complete. These tests were made by adding more molybdate solution, by allowing to stand at room temperature, and by reheating to 62°C. In all cases a precipitate formed but this action occurred most quickly in the filtrate that was reheated. In case of filtrates from determinations made on flour ash the precipitate was small in amount and took about 20 hours to form. The precipitates in filtrates from yeast ash formed within 1 hour.

Throughout this work the amount of molybdate solution used in each determination was the same—that is, for aliquots of flour ash, 20 cc. and for aliquots of yeast ash, 40 cc. This indicated that the trouble was due to a slow conversion of the meta and pyro phosphoric acids to the ortho phosphoric acid. It was evident that the 15 minutes specifically stated was not sufficient time for complete precipitation.

Another precipitation was made, the same procedure being followed except that the time was increased to 17 hours. Table 3 shows the results of the increased time for precipitation. The higher percentages of phosphoric acid are readily seen.

TABLE 3.  
*Results when precipitation time was increased to 17 hours.*

YEAST No. I.	YEAST No. II.
<i>per cent</i>	<i>per cent</i>
2.8120	1.9780
2.4410	2.0050
2.6730	2.2250
2.5650	2.3480
2.5490	1.9780
Average..	2.1070

The results in Table 3 show a gain of 0.4520 per cent phosphoric acid in case of yeast No. 1 and 0.4110 per cent for yeast No. II.

The filtrates from these determinations were also tested, and in each case additional precipitation took place.

From the foregoing work it seemed that either the time of precipitation should be extended considerably or a more rapid and complete conversion of phosphoric acid to ortho form should be effected. The rapid and complete conversion of phosphoric acid seemed the most desirable so the hydrochloric acid was increased to 2 cc., the solution was evaporated to dryness, and the same procedure was followed. Table 4 shows the results obtained.

In case of yeast No. I, a gain of 0.9010 per cent is noted over the preceding determination, and a gain of 1.185 per cent for yeast No. II.

TABLE 4.

*Results obtained by increasing amount of oxidizing agent and 17 hour period of precipitation.*

YEAST NO. I.	YEAST NO. II.
<i>per cent</i>	<i>per cent</i>
3.2710	3.631
3.6310	3.390
3.5070	3.013
3.4920	3.337
3.6460	3.090
Average.. 3.5090	3.292

The amount of hydrochloric acid was still further increased to 6 cc. and in addition 2 cc. of nitric acid was used. The solution was evaporated to dryness, and the time of the precipitation was increased to 20 hours; otherwise the procedure previously used was followed. The results are shown in Table 5.

TABLE 5.

*Results obtained by further increasing amount of acid used for conversion of the phosphoric acid and time of precipitation.*

YEAST NO. I.	YEAST NO. II.
<i>per cent</i>	<i>per cent</i>
3.7850	3.3370
3.8630	3.6150
3.9090	3.6150
3.8320	3.1520
3.8470	3.0900
Average.. 3.8470	3.3610

As in the preceding cases, tests showed that precipitation formed in each case, particularly when heated to 62° C. In the filtrates from the determinations given in Table 5, the precipitate was much less in amount than in any previous determination.

It seemed possible that the temperature of ashing might be influential in conversion of phosphoric acid to ortho form. Determinations were made at 600° C. on all samples except yeast No. II. This had to be omitted because of fusing at temperature above 450° C.

The ashes were dissolved in hydrochloric acid according to the official method, 5 (a), and the same procedure followed as previously outlined, without evaporation to dryness. This time the 15 minute precipitation period was used. Table 6 shows results of ash and phosphoric acid determinations.

The filtrates from determinations in Table 6 came through clear, but all had a precipitate formed within 4 hours.

TABLE 6.  
Results obtained by following official methods.

FLOUR No. 100		FLOUR No. 101		YEAST No. 1	
Ash	Phosphoric Acid	Ash	Phosphoric Acid	Ash	Phosphoric Acid
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0.4075	0.0494	0.6538	0.0680	10.0950	2.0390
0.3750	0.0494	0.6775	0.0680	9.8450	1.9780
0.3825	0.0433	0.6613	0.0803	9.6687	1.9620
0.3825	0.0562	0.6550	0.0618	10.0050	2.0390
0.3815	0.0494	0.6638	0.0803	9.9775	1.9160
Average 0.3858	0.0495	0.6620	0.0717	9.9182	1.9868

With another set of ash burned at 600° C., the treatment was varied. The ash was first dissolved in 1 cc. of hydrochloric; 6 cc. of nitric acid was added, and the solution evaporated to dryness. The procedure then followed was the same as used previously, except that the precipitation was made at room temperature for a period of 46 hours. Results of these determinations are shown in Table 7.

TABLE 7.  
Results obtained by ashing at 600° C., use of 1 cc. of hydrochloric acid and 6 cc. of nitric acid for conversion of phosphoric acid and 46 hour period of precipitation.

FLOUR No. 100.		FLOUR No. 101.		YEAST No. 1.	
<i>per cent</i>		<i>per cent</i>		<i>per cent</i>	
0.2132		0.3553		3.9240	
0.2132		0.3461		3.9550	
0.2287		0.3523		3.9240	
0.2008		0.3523		3.9090	
0.2256		0.3646		3.9240	
Average . . . 0.2163		0.3541		3.9272	

The figures in Table 7 are to be compared with those in Table 8, the results from ash burned at 550° C. and treated the same as those in Table 7, except that evaporation was carried to dryness with 2 cc. of hydrochloric acid.

TABLE 8.  
Results obtained by ashing at 550° C., use of 2 cc. hydrochloric acid and 6 cc. of nitric acid for conversion of the phosphoric acid and 46 hour period of precipitation.

FLOUR No. 100.		FLOUR No. 101.	
<i>per cent</i>		<i>per cent</i>	
0.1730		0.3337	
0.1823		0.3368	
0.1730		0.3306	
0.1669		0.3399	
0.1678		0.3274	
Average . . . . . 0.1766		0.3337	

TABLE 9.  
Summary of results.

MATERIAL	TEMPERATURE FOR ASHING	ASH-AVERAGE	PREPARATION OF SOLUTION	TIME OF PRECIPITATION	TEMPERATURE OF PRECIPITATION	PRO-AVERAGE	FILTRATE
Flour	°C.	per cent			°C.	per cent	
100	550	0.3918	Moistened with water, then dissolved in 1 cc. conc. HCl.	15 minutes	62	0.0451	Precipitate formed after heating and standing 24 hours.
101	550	0.6871	Moistened with water, then dissolved in 1 cc. conc. HCl.	15 minutes	62	0.0692	Precipitate formed after heating within 4 hours.
101	600	0.3858	Moistened with water, dissolved in 2 cc. HCl, brought to dryness.	46 hours	20	0.0495	Only very slight precipitate formed after heating and standing 48 hours.
101	550	0.6620				0.0717	
100	550	0.3918				0.1766	
101	550	0.6871				0.3337	
100	600	0.3858				0.2163	
101	600	0.6620				0.3541	
Dried Yeast							
I	550	10.0495	Moistened with water, then dissolved in 2 cc. HCl.	15 minutes	62	2.156	Precipitate formed within 1 hour.
II	450	6.5217				1.696	
I	550	10.0495	Moistened with water, then dissolved in 2 cc. HCl.	17 hours	20	2.608	Precipitate formed within 1 hour.
II	450	6.5217				2.107	
I	550	10.0495	Moistened with water, dissolved in 2 cc. HCl, brought to dryness.	15 minutes	62	3.509	Precipitate formed within 1 hour.
II	450	6.5217				3.292	
I	550	10.0495	Moistened with water, dissolved in 6 cc. HCl, brought to dryness.	20 hours	20	3.847	Precipitate formed but much less in amount than in any previous case.
II	450	6.5217				3.361	
I	600	9.9182	Moistened with water, dissolved in 2 cc. HCl.	15 minutes	62	1.9868	Precipitate formed within 4 hours.
I	600	9.9182	Moistened with water, dissolved in 2 cc. HCl, 6 cc. HNO <sub>3</sub> added, brought to dryness.	46 hours	20	3.9272	Only very slight precipitate formed after heating and standing 48 hours.

The filtrates from determinations in Tables 7 and 8 were tested; after standing at room temperature for 48 hours only, a very slight precipitate was formed in the filtrates from determination in Table 8. This precipitate was more of a film coat than a granular precipitate. In filtrates from determinations in Table 7 no precipitate or any cloudiness had formed until heated to 62°C. After 48 hours a very slight precipitate formed, one that would be considered within experimental error.

Table 9 shows the average results obtained in each set of determinations.

In examining the data given, it will be noted that when the flour ash on Sample No. 100 was moistened with water, dissolved in 2 cc. of hydrochloric acid, 6 cc. of nitric acid added, and then evaporated to dryness, 4.796 times as much phosphoric acid was obtained as when it was moistened with water and dissolved in 1 cc. of hydrochloric acid. With flour sample No. 101, the latter amount is 5.117 times the former amount.

In the case of dried yeast No. 1, the same change in method resulted in increasing the phosphoric acid content indicated 1.82 times.

From these data it seems obvious that more accurate and specific directions should be given in the official methods for the determination of phosphorus. The preparation of the solution from the ash is an important step, and the experiments made indicate that it is preferable to dissolve in concentrated hydrochloric acid, then to add 5-10 cc. of nitric acid, and to *evaporate to dryness*. This or some equivalent reaction is absolutely necessary in order to convert the meta and pyro phosphoric acid present to the ortho phosphoric acid form so that it can be precipitated by the molybdate solution.

It also appears that the 15 minutes allowed for precipitation is not sufficient for a complete formation of the ammonium phosphomolybdate in certain cases.

No advantage was obtained by ashing at 600° C. as compared with 550°C.

## CONTRIBUTED PAPERS.

### ANALYSES OF NOODLES OF KNOWN COMPOSITION AND ESTIMATION OF THEIR EGG SOLIDS CONTENT.

By RUTH BUCHANAN (Food Control Laboratory, Bureau of Chemistry,  
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#### INTRODUCTION.

Egg noodles are defined by the U. S. Department of Agriculture<sup>1</sup> as "dried alimentary pastes containing not less than 5 per cent by weight of the solids of whole, sound egg". In commercial practice noodles are made from either flour or semolina or mixtures of these with one of the following egg materials:

- (1) Liquid or frozen or dried whole egg;
- (2) Liquid or frozen or dried commercial yolk;
- (3) Mixtures of whole egg and commercial yolk; and
- (4) Mixtures of egg white and whole egg or commercial yolk.

Egg solids in a noodle are estimated at present almost universally from the lecithin-phosphoric acid content. As lecithin occurs in the yolk of the egg but not in the white, it offers a means of determining yolk but not the quantity of white accompanying the yolk. The presence of small amounts of lecithin in flour and semolina add further complications to this estimation. It has been found by Nockmann<sup>2</sup> and Hertwig<sup>3</sup> that the lecithin in a noodle decreases during manufacture and storage, and recent methods for lecithin indicate that the methods heretofore used give incomplete extraction.

In general, the present methods of analyzing noodles and the means of estimating the egg solids have been far from satisfactory, and strict reliance can not be placed upon the results. For these reasons this investigation was undertaken. The specific purposes were the following:

1. To assemble and test the most promising methods for determining whole egg as well as yolk solids in noodles.
2. To learn the composition of noodles containing known amounts of the various egg materials used commercially.
3. To ascertain the differences in noodles made with semolina and those made with flour, or mixtures of these, as base materials.

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<sup>1</sup> U. S. Dept. Agr. Circ. 136, Office of the Secretary, 1919.

<sup>2</sup> *Z. Nahr. Genussm.*, 1913, 25: 717.

<sup>3</sup> *J. Assoc. Official Agr. Chemists*, 1923, 7: 84, 91.

4. To determine the recovery from noodles of those substances of the ingredients that are used to estimate the egg solids.

5. To determine the effect of storage on the composition of noodles.

### HISTORICAL.

Bein<sup>1</sup> and Wichelhaus<sup>2</sup> were the first to estimate quantitatively egg yolk in foods. They determined the phosphoric acid in the alcohol and ether extract. Juckenack<sup>3</sup> used hot alcohol for this extraction; in other details his procedure was similar to that of Wichelhaus. Until recently, Juckenack's method has been considered most dependable for determining eggs in egg products. However, Rask, in an unpublished paper, Hertwig<sup>4</sup>, and others have shown that this method gives incomplete extraction. Rask<sup>5</sup> proposes digesting with hot ammoniacal alcohol and subsequent extraction with ether. The ammoniacal alcohol digestion apparently gives more complete extraction. Hertwig digests the sample with hot 70 per cent alcohol and then extracts with a mixture of alcohol and ether. The 70 per cent alcohol digestion permits more complete extraction by the subsequent ether-alcohol mixture. Grossfeld<sup>6</sup> and Hertwig<sup>7</sup> hydrolyze the sample with hot hydrochloric acid and then extract the fat from the resulting solution. Organic phosphoric acid is destroyed during the acid treatment.

Cappenberg<sup>8</sup>, and Berg and Angerhausen<sup>9</sup> propose cholesterol as a means of determining egg solids. This method has not been practically applied.

Attempts also have been made to estimate the egg content of noodles by determining the albumen present. Schmidt<sup>10</sup> extracts with water and precipitates albumen with 10 per cent nitric acid. Martin<sup>11</sup> uses acetic acid for this precipitation. Farcy<sup>12</sup> coagulates the albumen with heat. Arragon and Bornaud<sup>13</sup> propose the determination of egg white by means of an egg albumen precipitin serum. Gothe<sup>14</sup> claims that egg in noodles may be determined by a specific serum, and that it is possible thus to distinguish between egg white and egg yolk products. Thoni<sup>15</sup> finds that Gothe's method is applicable to fresh eggs, but not to dried or otherwise altered eggs, as it makes possible the detection of the white only. Schaffer and Gury<sup>16</sup> add cupric sulfate and sodium hydroxide to

<sup>1</sup> Ber., 1890, 23: 423.

<sup>2</sup> Analyst, 1890, 15: 116.

<sup>3</sup> Z. Nahr. Genussm., 1900, 3: 1.

<sup>4</sup> J. Assoc. Official Agr. Chemists, 1923, 7: 91.

<sup>5</sup> Ibid., 1922, 6: 61.

<sup>6</sup> Z. Nahr. Genussm., 1917, 24, 490.

<sup>7</sup> J. Assoc. Official Agr. Chemists, 1923, 6: 508.

<sup>8</sup> Chem. Ztg., 1909, 33: 985.

<sup>9</sup> Z. Nahr. Genussm., 1915, 29: 9.

<sup>10</sup> Chem. Ztg., 1912, 36: 796.

<sup>11</sup> Mon. Sci., 1921, 11, 151.

<sup>12</sup> Ann. fals., 1914, 7: 183.

<sup>13</sup> Chem. Ztg., 1913, 37: 1345.

<sup>14</sup> Z. Nahr. Genussm., 1915, 30: 389.

<sup>15</sup> Mitt. Lebens. Hyg., 1919, 10: 1.

<sup>16</sup> Chem. Zentr., 1916, Part 2: 431.

water extract of the paste and note the time required for the color to disappear. They find that the time required for the color to disappear in paste containing whole egg is longer than in paste containing yolk alone.

To distinguish between yolk and whole egg noodles, Hertwig<sup>1</sup> proposes ratios between fat by the acid hydrolysis method, lecithin phosphoric acid, and water-soluble protein-nitrogen precipitable by 40 per cent alcohol. Whole egg noodles contain decidedly more water-soluble protein-nitrogen precipitable by 40 per cent alcohol than noodles of similar yolk content or no eggs.

From the methods for analyzing noodles, mentioned previously, the following were chosen as the most applicable for this investigation:

Lipids and lipoid  $P_2O_5$  by the Rask-Phelps and Hertwig methods and the method of water-soluble protein-nitrogen precipitable by 40 per cent alcohol, as proposed by Hertwig.

#### OUTLINE OF INVESTIGATION.

Three classes of noodles, in batches of approximately 25 pounds each, were made at a noodle factory with semolina, flour, and a mixture of equal parts of each, respectively. The procedure of preparation was that usually followed. The kinds and amounts of egg material used with each class are summarized below. A total of 117 batches was made.

TABLE 1.  
*Egg solids in batches of each class.*

EGG MATERIAL	
(1) Dried whole egg.....	} Percentage of solids (dry basis) 2, 5, 8.
(2) Frozen whole egg.....	
(3) Dried yolk.....	
(4) Frozen yolk.....	
(5) 25% dried whole egg, 75% dried yolk.....	
(6) 25% frozen whole egg, 75% frozen yolk.....	
(7) 50% dried whole egg, 50% dried yolk.....	
(8) 50% frozen whole egg, 50% frozen yolk.....	
(9) 75% dried whole egg, 25% dried yolk.....	
(10) 75% frozen whole egg, 25% frozen yolk.....	
(11) 71% dried yolk, 29% dried albumen.....	
(12) 75% dried yolk, 25% dried albumen.....	
(13) 77% dried yolk, 23% dried albumen.....	

The dried whole egg and dried yolk were prepared from shell eggs, separated, and dried under the supervision of H. W. Redfield. The frozen eggs, both whole and yolk, were frozen in the presence of two members of the Bureau of Chemistry. The dried albumen, the flour, and the semolina were purchased on the market.

<sup>1</sup> *J. Assoc. Official Agr. Chemists*, 1923, 7: 84.



## PREPARATION OF NOODLES.

For the dried egg batches the requisite amount of egg material was run through a household flour sifter, water was added, and the mixture was well beaten for several minutes with an egg beater. After one-half hour the egg-water mixture and the base material were mixed in a machine for 6 to 10 minutes. The dough was placed in canvas and run through rollers until it became homogeneous. The canvas was removed and the dough reduced to a thickness of about 1-16 inch by passing through two rollers. It was then placed in another roll and fed to the cutting and folding machine. The finished noodles were dried in a room kept at a temperature of 110° F., with the humidity controlled by fans. The drying time varied from 16 to 18 hours. Care was taken to maintain the identity of all samples throughout the entire operation.

The batches made from dried yolk and dried albumen were prepared according to the above procedure. The frozen egg batches were made in a similar manner except that one hour was allowed for the egg to thaw before mixing, and no water was added. The finished noodles were packed in 5-pound boxes, sealed, and shipped by express to Washington.

## METHODS OF ANALYSIS.

*Moisture:* Association of Official Agricultural Chemists, Methods, 1920, page 71.

*Lipoids and lipoid  $P_2O_5$ :*

(a) Rask-Phelps. Journal Association of Official Agricultural Chemists, 1922, 6, 63.

(b) Hertwig. Journal Association of Official Agricultural Chemists, 1923, 7: 92.

(See modified method in report of the Referee on Eggs and Egg Products and adopted as tentative by the A. O. A. C. 1923.)

NOTE.—In determining the phosphoric acid in these methods it was precipitated with ammonium molybdate solution and allowed to stand overnight; otherwise the procedure was not changed. Precipitations of phosphoric acid in ten determinations made as indicated and as prescribed by the official method of heating, that is, for 15 minutes at 60–65° C., gave identical results.

*Total nitrogen:* Association of Official Agricultural Chemists, Methods, 1920, page 6.

*Water-soluble nitrogen:* Journal Association of Official Agricultural Chemists, 1923, 7: 85.

*Water-soluble protein-nitrogen precipitable by 40% alcohol:* Journal Association of Official Agricultural Chemists, 1923, 7: 85. (See modified method in report of Referee on Eggs and Egg Products and adopted as tentative by the A. O. A. C. 1923.)

## RESULTS.

Results of analyses; ratios between certain constituents helpful in identifying the kind of egg material present, multiplied by 100; percentage recovery in the noodles of those substances used in calculating egg solids; and the percentage of egg solids calculated from a general formula are given in Tables 4 to 6, inclusive. Analyses of the raw materials alone are given in Tables 2 and 3. Table 7 gives maximum and minimum values for semolinas, flours, eggs, and noodles made with whole egg and egg yolk.

TABLE 2.  
*Composition of semolina, flours, and semolina-flour mixture used in making noodles.*

SAMPLE	MOISTURE (Vacuum 100° C.)	LIPIDS		LIPID P <sub>2</sub> O <sub>5</sub>		TOTAL NITROGEN	WATER- SOLUBLE NITROGEN	40% ALCOHOL- PRECIP- ITABLE NITROGEN	RATIOS (Multiplied by 100)			
		Rask- Phelps	Hertwig	Rask Phelps	Hertwig				Alcohol- Precip- itable Total Nitrogen	Lipoid P <sub>2</sub> O <sub>5</sub> Alcohol- Precipitable Nitrogen	Alcohol- Precipitable Nitrogen Lipoids	
Semolina . . . . .	per cent 11.04	per cent 1.80	per cent 1.80	per cent 0.050	per cent 0.048	per cent 2.02	per cent 0.218	per cent 0.044	2.2	109.0	2.4	
Semolina . . . . .	11.09	1.87	1.85	0.050	0.049	1.95	0.218	0.044	2.3	111.3	2.4	
Semolina . . . . .	10.27	1.87	1.82	0.050	0.048	1.97	0.223	0.050	2.5	96.0	2.8	
Flour . . . . .	10.19	2.45	2.40	0.051	0.055	2.01	0.246	0.056	2.8	98.2	2.3	
Flour . . . . .	10.79	2.34	2.46	0.056	0.055	2.07	0.246	0.056	2.7	98.2	2.3	
Semolina 50%-flour 50%	10.20	2.20	2.23	0.052	0.050	2.04	0.238	0.053	2.6	94.3	2.4	

TABLE 3.  
*Composition of eggs used in making noodles (dry basis).*

SAMPLE	MOISTURE (Vacuum 100° C.)	LIPIDS		LIPID P <sub>2</sub> O <sub>5</sub>		TOTAL NITROGEN	WATER- SOLUBLE NITROGEN	40% ALCOHOL- PRECIP- ITABLE NITROGEN	RATIOS (Multiplied by 100)		
		Rask- Phelps	Hertwig	Rask- Phelps	Hertwig				Alcohol- Precip- itable Total Nitrogen	LIPID P <sub>2</sub> O <sub>5</sub> Alcohol- Precipitable Nitrogen	Alcohol- Precipitable Nitrogen Lipoids
Dried whole egg.....	per cent 4.57	per cent 44.96	per cent 44.96	per cent 1.28	per cent 1.26	per cent 7.57	per cent 4.30	per cent 3.57	47.20	35.3	7.9
Dried egg yolk.....	3.11	60.90	59.25	1.74	1.70	5.42	1.31	0.868	16.0	195.8	1.5
Dried egg white.....	10.08	.....	.....	.....	.....	12.47	10.59	9.24	.....	.....	.....
Frozen whole egg*.....	70.78	49.53	54.50	1.42	1.38	7.74	4.28	2.33	30.1	59.2	4.7
Frozen yolk*.....	54.93	54.57	65.95	1.76	1.72	5.90	1.98	0.546	9.3	315.0	0.83

\*These analyses were made by Max Ruderman of the New York Station, Bureau of Chemistry. Dried and frozen eggs were not made from same shell eggs.

TABLE  
Composition of noodles

SAMPLE NO.	BASE USED	EGG USED	ACTUAL EGG SOLIDS CONTENT (Dry basis)	MOISTURE (Vacuum 100°C.)	LIPOIDS		LIPOID P <sub>2</sub> O <sub>5</sub>		TOTAL NITROGEN
					Raak- Phelps	Hertwig	Raak- Phelps	Hertwig	
COMMERCIAL WHOLE									
1	Semolina.....	Dried egg.	2.14	9.39	2.70	2.65	0.074	0.072	2.29
40	Flour.....	Dried egg.	2.13	7.70	3.26	3.32	0.080	0.079	2.20
79	Semolina-flour	Dried egg.	2.12	8.35	3.07	3.11	0.076	0.074	2.23
16	Semolina.....	Frozen egg	2.33	8.95	2.79	2.85	0.078	0.075	2.13
55	Flour.....	Frozen egg	2.32	8.20	3.57	3.51	0.084	0.082	2.23
94	Semolina-flour	Frozen egg	2.31	8.86	3.15	3.27	0.079	0.076	2.23
COMMERCIAL									
4	Semolina.....	Dried egg.	2.17	9.08	2.96	2.97	0.082	0.082	2.22
43	Flour.....	Dried egg.	2.16	7.49	3.61	3.60	0.091	0.081	2.16
82	Semolina-flour	Dried egg.	2.15	8.15	3.40	3.40	0.085	0.082	2.13
19	Semolina.....	Frozen egg	2.34	8.50	2.94	3.16	0.082	0.080	2.10
58	Flour.....	Frozen egg	2.33	8.37	3.51	3.71	0.090	0.088	2.33
97	Semolina-flour	Frozen egg	2.32	8.87	3.25	3.49	0.084	0.082	2.19
75% COMMERCIAL WHOLE EGG SOLIDS.									
13	Semolina.....	Dried egg.	2.15	9.27	2.82	2.75	0.079	0.074	2.23
52	Flour.....	Dried egg.	2.14	8.11	3.45	3.44	0.084	0.082	2.23
91	Semolina-flour	Dried egg.	2.13	8.31	3.16	3.17	0.079	0.075	2.19
28	Semolina.....	Frozen egg	2.34	9.16	2.78	2.95	0.079	0.078	2.10
67	Flour.....	Frozen egg	2.33	8.17	3.37	3.43	0.088	0.087	2.27
106	Semolina-flour	Frozen egg	2.32	8.12	3.20	3.25	0.081	0.079	2.23
50% COMMERCIAL WHOLE EGG SOLIDS.									
10	Semolina.....	Dried egg.	2.16	8.97	2.85	2.82	0.076	0.074	2.16
49	Flour.....	Dried egg.	2.15	7.84	3.51	3.49	0.087	0.085	2.19
88	Semolina-flour	Dried egg.	2.14	8.01	3.25	3.27	0.082	0.079	2.16
25	Semolina.....	Frozen egg	2.34	8.64	2.90	2.92	0.083	0.078	2.13
64	Flour.....	Frozen egg	2.33	7.83	3.43	3.62	0.089	0.087	2.27
103	Semolina-flour	Frozen egg	2.32	8.43	3.21	3.41	0.082	0.080	2.20
25% COMMERCIAL WHOLE EGG SOLIDS.									
7	Semolina.....	Dried egg.	2.16	8.84	2.88	2.87	0.077	0.076	2.09
46	Flour.....	Dried egg.	2.15	7.59	3.55	3.55	0.087	0.089	2.21
85	Semolina-flour	Dried egg.	2.14	8.47	3.29	3.22	0.082	0.080	2.15
22	Semolina.....	Frozen egg	2.34	8.36	2.91	3.00	0.081	0.080	2.12
61	Flour.....	Frozen egg	2.33	8.14	3.41	3.66	0.087	0.085	2.24
100	Semolina-flour	Frozen egg	2.32	8.14	3.27	3.47	0.086	0.084	2.21
29% COMMERCIAL WHITE SOLIDS.									
31	Semolina.....	Dried egg.	2.13	8.77	2.65	2.64	0.070	0.070	2.31
70	Flour.....	Dried egg.	2.12	8.35	3.24	3.25	0.080	0.078	2.30
109	Semolina-flour	Dried egg.	2.11	8.15	3.06	3.06	0.075	0.073	2.26
25% COMMERCIAL WHITE SOLIDS.									
34	Semolina.....	Dried egg.	2.13	7.85	2.71	2.71	0.076	0.072	2.24
73	Flour.....	Dried egg.	2.12	8.01	3.28	3.31	0.081	0.079	2.23
112	Semolina-flour	Dried egg.	2.11	8.08	3.17	3.10	0.075	0.073	2.23
23% COMMERCIAL WHITE SOLIDS.									
37	Semolina.....	Dried egg.	2.13	8.21	2.77	2.69	0.078	0.075	2.13
76	Flour.....	Dried egg.	2.12	8.15	3.33	3.32	0.083	0.080	2.35
115	Semolina-flour	Dried egg.	2.11	8.53	3.10	3.08	0.079	0.076	2.22

NOTE.—The semolina-flour mixture contained 50% flour and 50% semolina.

4.  
(2% egg solids).

WATER-SOLUBLE NITROGEN	40% ALCOHOL-PRECIPI-TABLE NITROGEN	RATIOS (Multiplied by 100)			LIPOIDS RECOVERED		LIPOID P <sub>2</sub> O <sub>5</sub> RECOVERED		EGG SOLIDS (Dry Basis) CALCULATED BY GENERAL FORMULA FOR	
		Alcohol-Precipitable Nitrogen	Lipoid P <sub>2</sub> O <sub>5</sub>	Alcohol-Precipitable Nitrogen	Rank-Phelps	Hertwig	Rank-Phelps	Hertwig	Whole Egg Noodles	Egg Yolk Noodles
		Total Nitrogen	Alcohol-Precipitable Nitrogen	Lipoids						

## EGG SOLIDS.

per cent	per cent				per cent	per cent	per cent	per cent	per cent	per cent
0.316	0.100	4.4	72.0	3.8	100.0	95.8	99.1	100.1	2.4	.....
0.308	0.102	4.6	77.4	3.4	107.9	99.1	92.4	93.9	2.6	.....
0.350	0.113	5.0	65.5	3.6	98.6	99.1	95.8	98.1	2.6	.....
0.287	0.109	5.1	68.8	3.8	90.6	89.3	94.4	91.4	2.6	.....
0.356	0.108	4.8	75.9	3.1	92.7	92.2	92.2	88.8	3.2	.....
0.342	0.098	4.4	77.6	3.0	91.8	90.9	92.2	88.7	2.7	.....

## YOLK.

0.283	0.078	3.5	105.1	2.6	94.0	99.1	93.5	100.1	.....	2.5
0.286	0.070	3.2	115.7	1.9	96.8	100.0	99.0	94.0	.....	3.0
0.325	0.078	3.7	105.1	2.3	98.6	98.6	98.6	100.0	.....	2.5
0.269	0.067	3.2	119.4	2.1	93.6	94.5	85.5	84.6	.....	2.4
0.293	0.067	2.9	131.5	1.8	93.6	90.6	88.0	87.6	.....	3.0
0.338	0.079	3.6	103.8	2.3	91.4	90.4	86.2	87.9	.....	2.5

## 25% COMMERCIAL YOLK SOLIDS.

0.319	0.111	5.0	66.7	4.0	103.7	99.1	100.0	99.1	2.6	.....
0.297	0.110	4.9	73.9	3.2	99.5	99.1	100.0	90.2	3.2	.....
0.322	0.109	5.0	67.6	3.4	100.0	97.7	91.0	86.4	2.6	.....
0.283	0.106	5.0	73.6	3.6	87.6	93.6	91.0	94.4	3.1	.....
0.328	0.090	4.0	78.4	2.6	88.0	80.3	94.4	91.4	3.7	.....
0.322	0.095	4.3	71.2	2.9	91.0	80.6	88.8	92.2	3.0	.....

## 50% COMMERCIAL YOLK SOLIDS.

0.297	0.100	4.6	74.0	3.6	97.2	98.2	83.3	87.5	2.6	1.5
0.303	0.090	4.1	94.4	2.6	95.4	100.0	99.5	98.6	3.5	2.1
0.312	0.095	4.4	83.2	2.9	99.1	101.0	99.5	98.6	3.0	1.8
0.288	0.101	4.7	77.2	3.5	94.0	85.0	97.4	88.5	2.9	1.7
0.361	0.090	4.0	96.7	2.5	90.6	91.0	95.7	92.3	3.6	2.3
0.361	0.087	4.0	92.0	2.3	90.5	90.9	96.1	89.2	3.1	1.8

## 75% COMMERCIAL YOLK SOLIDS.

0.260	0.070	3.3	108.5	2.4	93.1	95.8	82.4	84.3	.....	2.0
0.297	0.081	3.7	109.8	2.3	99.5	99.1	100.9	103.0	.....	3.0
0.319	0.081	3.8	98.7	2.5	93.5	89.8	95.3	97.7	.....	2.4
0.283	0.078	3.7	102.5	2.6	92.7	85.9	84.2	86.8	.....	2.4
0.338	0.092	4.1	92.4	2.5	95.7	95.7	92.7	95.0	.....	2.7
0.365	0.084	3.8	100.0	2.4	93.1	90.9	95.7	95.7	.....	2.6

## 71% COMMERCIAL YOLK SOLIDS.

0.389	0.150	6.5	44.0	5.7	98.1	99.5	84.0	89.2	2.6	1.3
0.392	0.149	6.5	52.3	4.6	98.6	99.5	108.0	94.3	2.9	1.7
0.401	0.149	6.5	49.0	4.9	100.1	101.9	97.1	98.5	2.5	1.4

## 75% COMMERCIAL YOLK SOLIDS.

0.370	0.123	5.5	58.5	4.5	94.8	99.5	96.7	93.0	2.3	1.3
0.440	0.121	5.4	65.3	3.7	96.7	100.4	106.6	103.7	3.2	1.8
0.370	0.120	5.4	60.8	3.9	100.0	99.5	91.9	89.6	2.4	1.4

## 77% COMMERCIAL YOLK SOLIDS.

0.310	0.095	4.5	78.9	3.5	100.4	95.8	106.1	100.9	2.6	1.6
0.439	0.120	5.1	66.7	3.6	100.4	99.1	110.3	96.1	3.2	1.8
0.431	0.123	5.1	61.8	4.0	99.4	97.6	103.3	101.9	2.7	1.6

TABLE  
Composition of noodles

SAMPLE NO.	BASE USED	EGG USED	ACTUAL EGG SOLIDS CONTENT (Dry basis)	MOISTURE (Vacuum 100°C.)	LIPIDS		LIPID P <sub>2</sub> O <sub>5</sub>		TOTAL NITROGEN
					Rask- Phelps	Hertwig	Rask- Phelps	Hertwig	
COMMERCIAL WHOLE									
2	Semolina . . . . .	Dried egg . . . . .	5.63	8.90	3.80	3.84	0.111	0.107	2.40
41	Flour . . . . .	Dried egg . . . . .	5.62	7.60	4.56	4.60	0.116	0.112	2.37
80	Semolina-flour	Dried egg . . . . .	5.60	8.30	4.29	4.25	0.105	0.104	2.32
17	Semolina . . . . .	Frozen egg . . . . .	5.96	8.04	4.19	4.44	0.118	0.116	2.34
56	Flour . . . . .	Frozen egg . . . . .	5.94	7.99	4.76	5.03	0.122	0.120	2.41
95	Semolina-flour	Frozen egg . . . . .	5.92	8.42	4.56	4.76	0.120	0.116	2.40
COMMERCIAL									
5	Semolina . . . . .	Dried egg . . . . .	5.54	8.80	4.89	4.67	0.135	0.131	2.30
44	Flour . . . . .	Dried egg . . . . .	5.53	7.75	5.26	5.21	0.142	0.136	2.24
83	Semolina-flour	Dried egg . . . . .	5.51	8.15	4.98	5.00	0.134	0.131	2.22
20	Semolina . . . . .	Frozen egg . . . . .	5.97	8.13	4.74	5.03	0.137	0.134	2.21
59	Flour . . . . .	Frozen egg . . . . .	5.95	8.33	5.01	5.50	0.139	0.139	2.33
98	Semolina-flour	Frozen egg . . . . .	5.93	8.21	4.80	5.34	0.127	0.122	2.30
75% COMMERCIAL WHOLE EGG SOLIDS.									
14	Semolina . . . . .	Dried egg . . . . .	5.49	9.20	4.20	4.17	0.114	0.112	2.41
53	Flour . . . . .	Dried egg . . . . .	5.47	7.52	4.59	4.68	0.122	0.120	2.38
92	Semolina-flour	Dried egg . . . . .	5.45	8.28	4.59	4.48	0.119	0.118	2.32
29	Semolina . . . . .	Frozen egg . . . . .	5.94	9.05	4.33	4.56	0.128	0.119	2.12
68	Flour . . . . .	Frozen egg . . . . .	5.93	7.68	4.84	4.86	0.128	0.123	2.41
107	Semolina-flour	Frozen egg . . . . .	5.91	7.86	4.48	4.36	0.124	0.121	2.37
50% COMMERCIAL WHOLE EGG SOLIDS.									
11	Semolina . . . . .	Dried egg . . . . .	5.51	9.10	4.55	4.60	0.120	0.116	2.29
50	Flour . . . . .	Dried egg . . . . .	5.49	7.55	5.07	4.99	0.134	0.131	2.30
89	Semolina-flour	Dried egg . . . . .	5.47	8.38	4.69	4.65	0.124	0.121	2.19
26	Semolina . . . . .	Frozen egg . . . . .	5.96	9.21	4.48	4.64	0.124	0.120	2.27
65	Flour . . . . .	Frozen egg . . . . .	5.94	7.46	4.90	5.20	0.133	0.131	2.43
104	Semolina-flour	Frozen egg . . . . .	5.92	8.26	4.76	5.07	0.127	0.124	2.37
25% COMMERCIAL WHOLE EGG SOLIDS.									
8	Semolina . . . . .	Dried egg . . . . .	5.52	8.94	4.61	4.56	0.127	0.125	2.23
47	Flour . . . . .	Dried egg . . . . .	5.51	7.31	5.11	5.12	0.140	0.136	2.30
86	Semolina-flour	Dried egg . . . . .	5.49	8.02	4.92	4.88	0.131	0.127	2.29
23	Semolina . . . . .	Frozen egg . . . . .	5.96	8.59	4.55	4.85	0.132	0.128	2.26
62	Flour . . . . .	Frozen egg . . . . .	5.95	7.81	4.96	5.44	0.139	0.136	2.40
101	Semolina-flour	Frozen egg . . . . .	5.93	8.33	4.74	5.23	0.133	0.129	2.33
29% COMMERCIAL WHITE SOLIDS.									
32	Semolina . . . . .	Dried egg . . . . .	5.44	8.92	3.82	3.80	0.108	0.105	2.44
71	Flour . . . . .	Dried egg . . . . .	5.42	7.94	4.35	4.36	0.113	0.110	2.41
110	Semolina-flour	Dried egg . . . . .	5.40	8.08	4.26	4.30	0.107	0.103	2.37
25% COMMERCIAL WHITE SOLIDS.									
35	Semolina . . . . .	Dried egg . . . . .	5.45	7.97	3.96	3.93	0.109	0.105	2.49
74	Flour . . . . .	Dried egg . . . . .	5.44	7.99	4.66	4.54	0.115	0.112	2.47
113	Semolina-flour	Dried egg . . . . .	5.42	8.04	4.35	4.37	0.110	0.107	2.40
23% COMMERCIAL WHITE SOLIDS.									
38	Semolina . . . . .	Dried egg . . . . .	5.46	8.04	4.21	3.99	0.112	0.108	2.30
77	Flour . . . . .	Dried egg . . . . .	5.44	7.65	4.62	4.58	0.120	0.117	2.35
116	Semolina-flour	Dried egg . . . . .	5.43	8.09	4.42	4.32	0.114	0.110	2.43

NOTE.—The semolina-flour mixtures contained 50% flour and 50% semolina.

5.  
(5% egg solids).

WATER-SOLUBLE NITROGEN	40% ALCOHOL-PRECIPTABLE NITROGEN	RATIOS (Multiplied by 100)			LIPIDS RECOVERED		LIPOID P <sub>2</sub> O <sub>5</sub> RECOVERED		EGG SOLIDS (Dry Base) CALCULATED BY GENERAL FORMULA FOR	
		Alcohol-Precipitable Nitrogen	Lipoid P <sub>2</sub> O <sub>5</sub>	Alcohol-Precipitable Nitrogen	Raak-Phelps	Hertwig	Raak-Phelps	Hertwig	Whole Egg Noodles	Egg Yolk Noodles
		Total Nitrogen	Alcohol-Precipitable Nitrogen	Lipoids						

## EGG SOLIDS.

per cent	per cent				per cent	per cent	per cent	per cent	per cent	per cent
0.411	0.160	6.7	66.9	4.2	87.4	90.2	95.7	92.7	5.7	.....
0.403	0.160	6.8	70.0	3.5	92.9	89.3	93.6	91.3	6.0	.....
0.437	0.205	8.8	61.6	4.1	93.2	89.6	83.4	83.2	5.2	.....
0.454	0.215	9.1	54.0	4.8	88.4	89.3	88.6	91.8	6.3	.....
0.490	0.203	9.2	53.8	4.4	89.5	89.7	85.7	87.5	6.6	.....
0.504	0.221	10.9	52.5	4.6	90.3	86.2	90.5	88.0	6.4	.....

## YOLK.

0.308	0.078	3.4	167.9	1.7	101.2	97.3	98.4	98.7	.....	6.0
0.313	0.070	3.1	194.3	1.3	93.8	94.0	98.2	93.8	.....	6.2
0.327	0.076	3.4	172.4	1.5	91.8	94.0	94.9	96.0	.....	5.9
0.297	0.078	3.5	171.8	1.5	99.0	89.9	91.5	92.8	.....	6.1
0.364	0.089	3.8	156.1	1.6	90.1	87.3	88.1	90.9	.....	6.5
0.364	0.092	4.0	132.6	1.7	89.7	87.7	81.3	80.1	.....	5.3

## 25% COMMERCIAL YOLK SOLIDS.

0.389	0.152	6.3	73.7	3.6	99.5	99.8	88.9	89.6	6.0	.....
0.398	0.163	6.8	73.6	3.4	90.1	93.8	87.8	88.9	6.6	.....
0.400	0.166	7.2	71.0	3.7	100.2	94.9	91.6	95.4	6.6	.....
0.389	0.151	7.1	78.8	3.3	93.3	90.4	98.3	92.3	6.6	.....
0.426	0.149	5.8	87.9	2.9	89.7	78.8	88.5	85.7	6.9	.....
0.418	0.151	6.4	80.1	3.4	84.0	68.7	89.7	92.7	6.7	.....

## 50% COMMERCIAL YOLK SOLIDS.

0.352	0.157	6.9	73.9	3.4	104.9	105.8	94.7	94.2	6.5	5.0
0.353	0.140	5.8	93.5	2.8	101.4	99.1	103.2	96.7	7.6	5.9
0.353	0.101	4.6	119.8	2.2	96.4	93.2	97.0	97.5	6.8	5.2
0.369	0.151	6.7	79.4	3.3	96.3	88.6	94.8	87.4	6.8	5.2
0.424	0.154	6.3	85.0	3.1	89.1	84.8	89.2	85.2	7.6	5.9
0.409	0.151	6.4	82.1	3.0	92.8	88.4	87.9	89.1	7.0	5.4

## 75% COMMERCIAL YOLK SOLIDS.

0.328	0.092	4.1	136.9	2.0	99.1	100.3	95.5	97.8	.....	5.6
0.342	0.081	3.5	167.8	1.6	94.7	96.2	102.0	95.3	.....	6.2
0.364	0.109	4.8	116.5	2.2	96.7	96.2	97.3	97.5	.....	5.6
0.319	0.117	5.2	109.4	2.4	95.7	89.6	90.9	91.6	.....	5.7
0.370	0.098	4.1	138.8	1.8	89.6	88.7	91.4	86.0	.....	6.2
0.370	0.131	5.6	98.4	2.5	89.9	89.0	90.4	91.0	.....	5.8

## 71% COMMERCIAL YOLK SOLIDS.

0.454	0.202	8.3	52.0	5.3	95.0	97.8	96.3	97.1	5.3	4.1
0.547	0.205	8.5	53.7	4.7	92.8	94.7	94.1	85.6	5.8	4.5
0.448	0.157	6.6	65.5	3.7	98.5	102.0	90.7	89.8	5.1	3.9

## 75% COMMERCIAL YOLK SOLIDS.

0.454	0.202	8.1	52.0	5.1	94.3	96.5	91.6	90.5	5.2	4.1
0.479	0.198	8.1	56.3	4.5	101.8	97.8	92.1	84.0	5.8	4.5
0.483	0.258	10.8	41.2	4.3	96.9	98.9	92.1	91.2	5.5	4.2

## 77% COMMERCIAL YOLK SOLIDS.

0.456	0.162	7.0	66.7	4.0	102.9	96.3	94.1	91.9	5.5	4.3
0.439	0.190	8.1	61.6	4.1	96.5	96.5	96.5	88.8	6.4	4.9
0.563	0.222	11.19	49.6	4.3	97.4	93.9	94.9	91.9	5.8	4.5

TABLE  
Composition of noodles

Composition of products									
SAMPLE NO.	BASE USED	EGG USED	ACTUAL EGG SOLIDS CONTENT (Dry basis)	MOISTURE (Vacuum 100°C.)	LIPOIDS		LIPID P <sub>2</sub> O <sub>5</sub>		TOTAL NITROGEN
					Rask- Phelps	Hertwig	Rask- Phelps	Hertwig	
COMMERCIAL WHOLE									
3	Semolina.....	Dried egg.	8.52	8.73	4.97	5.21	0.145	0.142	2.60
42	Flour.....	Dried egg.	8.49	7.63	5.78	5.82	0.158	0.152	2.49
81	Semolina-flour	Dried egg.	8.46	8.17	5.62	5.62	0.149	0.146	2.49
57	Flour.....	Frozen egg	9.21	8.13	6.23	6.57	0.164	0.161	2.58
96	Semolina-flour	Frozen egg	9.19	8.11	6.01	6.41	0.161	0.157	2.57
COMMERCIAL									
6	Semolina.....	Dried egg.	8.63	8.50	6.57	6.35	0.181	0.179	2.38
45	Flour.....	Dried egg.	8.61	7.29	7.15	7.20	0.191	0.187	2.38
84	Semolina-flour	Dried egg.	8.59	8.13	6.85	6.70	0.186	0.180	2.33
21	Semolina.....	Frozen egg	9.27	8.31	6.11	6.84	0.190	0.185	2.28
60	Flour.....	Frozen egg	9.25	7.89	6.54	7.87	0.194	0.192	2.44
99	Semolina-flour	Frozen egg	9.22	7.99	6.38	7.35	0.188	0.180	2.40
75% COMMERCIAL WHOLE EGG SOLIDS.									
15	Semolina.....	Dried egg.	8.55	8.79	5.53	5.61	0.146	0.145	2.55
54	Flour.....	Dried egg.	8.52	7.83	6.20	6.14	0.163	0.161	2.53
93	Semolina-flour	Dried egg.	8.50	8.12	5.97	5.92	0.160	0.156	2.46
30	Semolina.....	Frozen egg	9.25	8.80	5.65	6.37	0.163	0.155	2.19
69	Flour.....	Frozen egg	9.22	7.91	6.28	6.33	0.174	0.169	2.81
108	Semolina-flour	Frozen egg	9.19	7.63	6.12	6.59	0.166	0.162	2.53
50% COMMERCIAL WHOLE EGG SOLIDS.									
12	Semolina.....	Dried egg.	8.58	8.78	5.89	5.60	0.168	0.165	2.46
51	Flour.....	Dried egg.	8.55	7.69	6.58	6.54	0.176	0.172	2.43
90	Semolina-flour	Dried egg.	8.53	8.11	6.35	6.23	0.168	0.162	2.44
27	Semolina.....	Frozen egg	9.26	8.99	5.68	6.34	0.175	0.170	2.38
66	Flour.....	Frozen egg	9.23	7.47	6.41	6.80	0.179	0.174	2.50
105	Semolina-flour	Frozen egg	9.21	7.91	6.22	6.89	0.174	0.169	2.52
25% COMMERCIAL WHOLE EGG SOLIDS.									
9	Semolina.....	Dried egg.	8.61	8.63	6.20	6.21	0.176	0.165	2.34
48	Flour.....	Dried egg.	8.59	7.32	6.75	6.77	0.187	0.183	2.46
87	Semolina-flour	Dried egg.	8.56	8.22	6.58	6.61	0.175	0.172	2.41
24	Semolina.....	Frozen egg	9.26	8.18	6.07	6.79	0.181	0.175	2.31
63	Flour.....	Frozen egg	9.24	7.38	6.55	7.32	0.187	0.183	2.49
102	Semolina-flour	Frozen egg	9.22	7.90	6.31	7.09	0.182	0.177	2.47
29% COMMERCIAL WHITE SOLIDS.									
33	Semolina.....	Dried egg.	8.47	7.72	5.19	5.09	0.142	0.138	2.63
72	Flour.....	Dried egg.	8.45	7.81	5.68	5.59	0.147	0.144	2.61
111	Semolina-flour	Dried egg.	8.42	7.73	5.58	5.55	0.140	0.135	2.58
25% COMMERCIAL WHITE SOLIDS.									
36	Semolina.....	Dried egg.	8.48	7.87	5.47	5.22	0.149	0.144	2.48
75	Flour.....	Dried egg.	8.47	7.77	5.88	5.82	0.151	0.148	2.55
114	Semolina-flour	Dried egg.	8.45	7.78	5.66	5.64	0.146	0.141	2.53
23% COMMERCIAL WHITE SOLIDS.									
39	Semolina.....	Dried egg.	8.50	8.08	5.66	5.32	0.152	0.147	2.44
78	Flour.....	Dried egg.	8.48	8.19	5.79	5.81	0.158	0.155	2.53
117	Semolina-flour	Dried egg.	8.45	7.99	5.80	5.58	0.152	0.146	2.51

NOTE.—The semolina-flour mixtures contained 50% flour and 50% semolina.

6.

(8% egg solids).

WATER-SOLUBLE NITROGEN	40% ALCOHOL-PRECIPI-TABLE NITROGEN	RATIOS (Multiplied by 100)			LIPIDS RECOVERED		LIPID P <sub>2</sub> O <sub>5</sub> RECOVERED		EGG SOLIDS (Dry Basis) CALCULATED BY GENERAL FORMULA FOR	
		Alcohol-Precipi-table Nitro-gen	Lipoid P <sub>2</sub> O <sub>5</sub> Precipi-table Nitrogen	Alcohol-Precipi-table Nitro-gen Lipoids	Raak-Phelps	Hertwig	Raak-Phelps	Hertwig	Whole Egg Noodles	Egg Yolk Noodles
		Total Nitro-gen								

## EGG SOLIDS.

per cent	per cent				per cent	per cent	per cent	per cent	per cent	per cent
0.507	0.260	10.0	54.6	5.0	92.7	92.1	98.8	99.3	8.8	.....
0.482	0.233	9.4	65.2	4.0	99.8	100.1	104.5	105.5	9.5	.....
0.529	0.246	9.9	59.4	4.4	101.9	100.8	100.6	99.5	9.0	.....
0.647	0.319	12.4	50.5	4.9	107.9	105.7	97.9	99.8	10.3	.....
0.619	0.300	11.7	52.3	4.9	89.7	82.8	89.7	90.6	10.0	.....

## YOLK.

0.338	0.109	4.6	164.2	1.7	100.8	99.2	97.5	100.0	.....	8.9
0.350	0.087	3.7	214.9	1.2	100.3	103.7	99.0	99.3	.....	9.2
0.364	0.093	4.0	193.5	1.4	99.7	98.3	99.7	99.2	.....	8.9
0.339	0.101	4.4	183.1	1.5	94.6	91.5	95.6	96.1	.....	9.2
0.409	0.120	4.9	160.0	1.5	92.2	99.7	96.3	98.7	.....	9.6
0.397	0.131	5.5	137.4	1.8	92.9	93.8	92.4	92.5	.....	8.9

## 25% COMMERCIAL YOLK SOLIDS.

0.479	0.243	9.5	59.7	4.3	99.8	103.4	84.2	87.4	9.1	.....
0.493	0.224	8.9	71.2	3.7	102.7	101.1	93.1	94.9	10.0	.....
0.484	0.221	9.0	70.6	3.7	102.0	100.7	94.6	95.6	10.0	.....
0.451	0.213	9.7	72.3	3.3	91.9	96.5	91.4	89.2	10.0	.....
0.476	0.213	7.6	79.3	3.3	93.3	82.5	94.4	91.4	11.1	.....
0.532	0.227	9.0	71.4	3.4	93.6	91.8	91.1	91.9	10.4	.....

## 50% COMMERCIAL YOLK SOLIDS.

0.428	0.176	7.2	93.8	3.1	100.6	95.5	102.5	103.7	10.9	7.9
0.431	0.143	5.9	120.2	2.2	103.7	103.7	103.7	98.8	11.3	8.3
0.411	0.168	6.9	96.4	2.7	103.7	99.5	101.3	99.2	10.1	7.6
0.465	0.182	7.6	93.4	2.9	90.6	91.5	102.5	96.1	11.4	8.3
0.476	0.143	5.7	121.7	2.1	93.4	87.5	92.3	88.5	11.5	8.4
0.460	0.182	7.2	92.9	2.6	94.1	94.2	93.0	92.5	11.0	8.0

## 75% COMMERCIAL YOLK SOLIDS.

0.328	0.128	5.5	128.9	2.0	100.1	103.0	100.3	96.0	.....	7.9
0.392	0.100	4.0	183.0	1.5	98.7	100.8	103.2	96.3	.....	8.6
0.392	0.151	6.2	113.9	2.3	101.0	103.2	98.8	99.8	.....	8.3
0.392	0.160	6.9	109.3	2.3	95.9	94.8	93.7	93.8	.....	8.5
0.468	0.160	6.4	114.3	2.1	93.8	93.0	93.0	90.0	.....	8.9
0.412	0.131	5.3	135.1	1.8	93.7	93.1	93.6	93.7	.....	8.6

## 71% COMMERCIAL YOLK SOLIDS.

0.552	0.246	9.4	50.1	4.8	102.0	102.6	97.8	98.1	8.3	5.5
0.606	0.269	10.3	53.5	4.8	101.5	100.7	96.5	92.2	8.8	5.9
0.689	0.263	10.2	51.3	4.7	104.5	106.5	94.4	92.6	8.0	5.3

## 75% COMMERCIAL YOLK SOLIDS.

0.532	0.255	10.3	56.5	4.8	104.9	100.9	100.4	99.0	8.8	5.9
0.505	0.249	9.8	59.4	4.3	101.6	101.7	96.3	91.3	9.1	6.1
0.490	0.288	11.4	49.0	5.1	100.8	102.1	95.3	94.6	8.5	5.7

## 77% COMMERCIAL YOLK SOLIDS.

0.465	0.250	10.2	58.8	4.7	107.5	101.2	100.8	99.3	9.1	6.1
0.535	0.252	10.0	61.5	4.3	96.8	99.5	100.7	108.4	9.8	6.6
0.569	0.274	10.9	53.3	4.9	102.2	97.8	98.8	97.1	9.1	6.0



TABLE  
Maximum and minimum results of semolinas, flours,

	ACTUAL EGG SOLIDS CONTENT (Dry basis)	MOISTURE (Vacuum 100°C.)	LIPIDS		LIPOID P <sub>2</sub> O <sub>5</sub>		TOTAL NITROGEN
			Rask- Phelps	Hertwig	Rask- Phelps	Hertwig	
SEMO							
Maximum.....	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Minimum.....	....	11.09	1.87	1.85	0.050	0.049	2.02
	....	10.27	1.80	1.80	0.050	0.048	1.95
FLO							
Maximum.....	....	10.79	2.45	2.46	0.056	0.055	2.07
Minimum.....	....	10.19	2.34	2.40	0.051	0.055	2.01
WHOLE EGG							
Maximum.....	....	....	49.53	54.50	1.42	1.38	7.74
Minimum.....	....	....	44.96	44.96	1.28	1.26	7.57
EGG YOLK							
Maximum.....	....	....	60.90	65.95	1.76	1.72	5.90
Minimum.....	....	....	54.57	59.25	1.74	1.70	5.42
2% WHOLE							
Maximum.....	2.33	9.39	3.57	3.51	0.088	0.082	2.29
Minimum.....	2.12	7.70	2.70	2.65	0.074	0.072	2.13
2% EGG							
Maximum.....	2.34	9.08	3.61	3.71	0.091	0.088	2.33
Minimum.....	2.15	7.49	2.94	2.97	0.082	0.080	2.10
5% WHOLE							
Maximum.....	5.96	8.90	4.76	5.03	0.122	0.120	2.41
Minimum.....	5.60	7.60	3.80	3.84	0.105	0.104	2.32
5% EGG							
Maximum.....	5.97	8.80	5.26	5.50	0.142	0.139	2.33
Minimum.....	5.51	7.75	4.74	4.67	0.127	0.122	2.21
8% WHOLE							
Maximum.....	9.21	8.73	6.23	6.57	0.164	0.161	2.60
Minimum.....	8.46	7.63	4.97	5.21	0.145	0.142	2.49
8% EGG							
Maximum.....	9.27	8.50	7.15	7.87	0.194	0.192	2.44
Minimum.....	8.59	7.29	6.11	6.35	0.181	0.179	2.29

7.

eggs, and noodles.

WATER-SOLUBLE NITROGEN	40 % ALCOHOL- PRECIPITABLE NITROGEN	RATIOS (Multiplied by 100)			LIPOIDS RECOVERED		LIPOID P <sub>2</sub> O <sub>5</sub> RECOVERED	
		Alcohol- Precipi- table Nitrogen Total Nitrogen	Lipoid P <sub>2</sub> O <sub>5</sub> Alcohol- Precipi- table Nitrogen	Alcohol- Precipi- table Nitrogen Lipoids	Rask- Phelps	Hertwig	Rask- Phelps	Hertwig
LINA.								
<i>per cent</i>	<i>per cent</i>				<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0.223	0.050	2.5	111.3	2.8	....	....	....	....
0.218	0.044	2.2	96.0	2.4	....	....	....	....
UR								
0.246	0.056	2.8	98.2	2.3	....	....	....	....
0.246	0.056	2.7	98.2	2.3	....	....	....	....
(dry basis).								
4.30	3.57	47.2	59.2	7.9	....	....	....	....
4.28	2.33	30.1	35.3	4.7	....	....	....	....
(dry basis).								
1.98	0.868	16.0	315.0	1.5	....	....	....	....
1.31	0.546	9.3	195.8	0.83	....	....	....	....
EGG NOODLES.								
0.356	0.113	5.1	77.5	3.8	107.9	99.0	99.0	100.0
0.287	0.098	4.4	65.5	3.0	90.5	89.2	92.2	88.7
YOLK NOODLES.								
0.338	0.079	3.7	131.5	2.6	98.6	100.0	99.0	100.0
0.269	0.067	2.9	103.8	1.8	91.3	90.4	85.4	84.6
EGG NOODLES.								
0.504	0.221	10.9	70.0	4.8	93.2	90.2	95.7	92.7
0.403	0.160	6.7	52.5	3.5	87.3	86.2	83.4	83.2
YOLK NOODLES.								
0.364	0.092	4.0	194.3	1.7	101.2	97.3	98.4	98.7
0.297	0.070	3.1	132.6	1.3	89.7	87.3	81.3	80.1
EGG NOODLES.								
0.647	0.319	12.4	65.2	5.0	107.9	105.7	104.5	105.5
0.482	0.233	9.4	50.5	4.0	89.7	82.8	89.7	90.6
YOLK SOLIDS.								
0.409	0.131	5.5	214.9	1.8	100.8	103.7	99.7	100.0
0.338	0.087	3.7	137.4	1.2	92.2	91.5	92.4	92.5

TABLE  
*Analyses of noodles at diff*

SAMPLE NO.	TIME ANALYZED	ACTUAL EGG SOLIDS CONTENT (Dry basis)	MOISTURE (Vacuum 100° C.)	LIPIDS		LIPOID P <sub>2</sub> O <sub>5</sub>	
				Rask-Phelps	Hertwig	Rask-Phelps	Hertwig
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
2	December, 1922 . . .	5.63	8.90	3.80	3.84	0.111	0.107
2	December, 1923 . . .	5.63	8.43	3.84	3.75	0.087	0.084
5	December, 1922 . . .	5.54	8.80	4.89	4.67	0.135	0.131
5	December, 1923 . . .	5.54	8.80	4.63	4.60	0.103	0.098
14	December, 1922 . . .	5.49	9.20	4.20	4.17	0.114	0.112
14	December, 1923 . . .	5.49	9.96	4.30	4.20	0.091	0.089
41	January, 1923 . . . .	5.62	7.50	4.56	4.60	0.112	0.116
41	December, 1923 . . .	5.62	9.44	4.19	4.08	0.086	0.090
41*	December, 1923 . . .	5.62	9.16	4.08	4.01	0.084	0.091
44	January, 1923 . . . .	5.53	7.75	5.26	5.21	0.142	0.136
44	December, 1923 . . .	5.53	9.41	4.94	5.00	0.109	0.107
44*	December, 1923 . . .	5.53	8.88	5.04	4.99	0.107	0.106

\*Unground sample stored in open paper boxes in basement.

Values in the tables under the caption "Actual egg solids content, dry basis" were calculated from the composition of the raw materials and the formulas of preparation. The values under the captions "Lipoids recovered" and "Lipoid P<sub>2</sub>O<sub>5</sub> recovered" were calculated from the analyses of the raw materials, the finished noodles, and from the factory formulas of preparation. Under the caption "Egg solids calculated by general formula on dry basis", the formulas used were recommended by Hertwig in his report on eggs and egg products at the November, 1923, meeting of the Association of Official Agricultural Chemists. The formulas and basic values recommended by him are as follows:

0.055% = lipid P<sub>2</sub>O<sub>5</sub> of flours, average value (dry basis).

1.38% = lipid P<sub>2</sub>O<sub>5</sub> of whole eggs, average value (dry basis).

1.78% = lipid P<sub>2</sub>O<sub>5</sub> of commercial yolk, average value (dry basis).

A = percentage of lipid P<sub>2</sub>O<sub>5</sub> in noodle sample (dry basis) multiplied by 1.1 (1.1 to account for loss of the lipid P<sub>2</sub>O<sub>5</sub> of ingredients during manufacture).

$$\frac{(A - 0.055) 100}{1.38 - 0.055} \text{ or}$$

(A - 0.055) 75.5 = percentage of whole egg solids in noodles on dry basis.

Likewise with samples for commercial yolk:

(A - 0.055) 58.0 = percentage of commercial yolk solids in dry noodle sample.

#### EFFECT OF STORAGE ON COMPOSITION OF NOODLES.

In Table 8, for comparative purposes, are given the composition of seven noodles, as analyzed shortly after preparation and after approximately one year of storage. During the storage period, five of the

8.

*erent periods during storage.*

TOTAL NITROGEN	WATER- SOLUBLE NITROGEN	40% ALCOHOL- PRECIPITABLE NITROGEN	RATIOS (Multiplied by 100)			EGG SOLIDS (Dry Basis) CALCULATED BY GENERAL FORMULA FOR	
			Alcohol- Precipitable Nitrogen Total Nitrogen	Lipoid $P_2O_5$ Alcohol- Precipitable Nitrogen	Alcohol- Precipitable Nitrogen Lipoids	Whole Egg Noodles	Egg Yolk Noodles
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>				<i>per cent</i>	<i>per cent</i>
2.40	0.411	0.160	6.7	66.9	4.2	5.7	...
2.41	0.396	0.151	6.3	55.6	4.0	3.5	...
2.30	0.308	0.078	3.4	167.9	1.7	...	6.0
2.24	0.299	0.067	3.0	146.3	1.5	...	3.6
2.41	0.389	0.152	6.3	73.6	3.6	6.04	....
2.37	0.367	0.132	5.6	67.4	3.1	4.18	...
2.37	0.403	0.160	6.8	70.0	3.5	6.0	...
2.29	0.370	0.154	6.7	58.5	3.8	4.1	...
2.29	0.395	0.146	6.4	62.3	2.6	4.1	....
2.24	0.313	0.070	3.1	194.3	1.3	...	6.20
2.21	0.297	0.060	2.7	178.3	1.2	...	3.8
2.21	0.311	0.056	2.5	189.2	1.1	....	3.5

samples were held in the ground condition in sealed Mason jars in the laboratory, and two samples were kept in paper cartons exposed to the air in the basement.

In all the determinations for lipoids and lipid  $P_2O_5$  Hertwig's values were used.

#### SUMMARY AND CONCLUSIONS.

1. Analyses are given of noodles containing known amounts of various egg materials and of their ingredients.

2. Noodles made from semolina or flour, or mixture of these and of the same egg content are of very similar composition.

3. The most promising methods for determining egg solids in noodles were found to be lipoids, lipid  $P_2O_5$ , total nitrogen, and water-soluble protein-nitrogen precipitable by 40 per cent alcohol.

4. Ratios between certain of these substances, multiplied by 100, as proposed by Hertwig, clearly distinguish between whole egg and yolk noodles and also between these and flours and semolinas.

5. The recovery in the whole egg and yolk noodles of the lipid  $P_2O_5$  of the ingredients ranged from 81.3 to 104.5 per cent by the Rask-Phelps method and 80.1 to 105.5 per cent by the Hertwig method. Low recovery in many instances may be accounted for by decomposition of the lipid  $P_2O_5$  during the lapse of time between manufacture and analysis.

6. The general formulas used for calculating egg solids, with the factor 1.1 to overcome loss of lipid  $P_2O_5$  during manufacture, as pro-

posed by Hertwig, give a close approximation to the actual whole egg and yolk solids content.

7. Seven samples of noodles analyzed before and after approximately a year of storage showed considerable loss in lipoid  $P_2O_5$ . The losses occurring in the ground samples stored in sealed Mason jars were similar to those occurring in the noodles held in their original condition in paper boxes in the basement. Little change took place in the water-soluble protein-nitrogen precipitable by 40 per cent alcohol. These losses must be taken into account in estimating the egg solids content of noodles of considerable age.

#### ACKNOWLEDGMENT.

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## THE DETERMINATION OF ESSENTIAL OILS IN CERTAIN FLAVORING EXTRACTS, AND OF CAMPHOR OR PEPPERMINT OIL IN CERTAIN PHARMACEUTICAL PREPARATIONS.

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A method for the determination of camphor and of certain essential oils when in solution in alcohol was published by Penniman and Randall<sup>1</sup> in 1914. In this article it was shown that results much more accurate than could be obtained by any other method known to the writers could be secured with the aid of even uncalibrated Babcock 10 per cent milk-test bottles, provided a redistilled gasoline boiling between 40° and 60° C. is employed as extracting solvent.

In brief, the method is as follows:

Precipitate (in a Babcock milk-test bottle) the essential oil or the camphor from its solution in alcohol by the addition of a strong, acidified calcium chloride solution; add a known volume of low-boiling gasoline and shake and centrifuge the mixture; add more calcium chloride solution to bring the gasoline-oil solution into the graduated part of the bottle neck and, after further shaking and centrifuging, note the volume of this gasoline-oil solution. On the assumption that the volume of this solution is equal to the sum of the volumes of gasoline and oil—an assumption which, within clear limits, seems to be justified—the volume of the oil can be calculated.

### DIFFICULTIES IN EARLIER WORK.

In the earlier work ordinary 10 per cent Babcock milk-test bottles were employed; later, calibrated 8 per cent bottles were used, and various inaccuracies and anomalies were found to disappear. The average of the highest and lowest points of the upper meniscus was taken as the true upper reading. Similarly, should temperature changes have caused the surface separating the supernatant and the subnatant liquid to take on a meniscus form, the highest and lowest points of this curved surface also were noted, and their average was used as the lower limit of the gasoline-oil column.

Again, it was found that pipets graduated to deliver certain exact volumes of water could not be depended upon to deliver corresponding volumes of gasoline. Accordingly, special pipets were made of thick-walled, narrow-bore tubing, with long drawn-out tips, bent and filed flat so as to deliver the gasoline smoothly against the inner wall of the test-bottle neck. These pipets were marked at the proper point after tests had shown that they delivered the volume of gasoline desired, as determined with the aid of the graduation of a calibrated test bottle.

<sup>1</sup> *J. Ind. Eng. Chem.*, 1914, 6: 926.



Thus, a 1 cc. pipet, so constructed and marked, would deliver such a volume of gasoline that, after the latter had been run into a bottle containing, say, 10 cc. of alcohol and the necessary amount of calcium chloride solution, and after the mixture had been shaken violently and centrifuged, the gasoline layer would occupy exactly 5 whole per cent divisions of the graduated neck.

Another source of difficulty in the earlier work—the formation of a white “collar” of flocculent material at the lower surface of the gasoline column—which at times interfered with the accurate determination of the position of this surface, was removed through the employment of a somewhat less concentrated calcium chloride solution to which about 4 per cent of its volume of concentrated hydrochloric acid had been added. Any alkalinity of the calcium chloride solution was thus overcome and, as a rule, a perfectly flat, clearly defined surface separated the gasoline from the subnatant liquid, since no light calcium salts were set free in insoluble form.

The gasoline used in this work has consisted of components boiling between 40° and 65° C., obtained through the fractional distillation of 88° Baumé material. The still consists of a copper lemon-oil can to which is fitted a glass tube about 4 feet long, containing a close coil of iron wire; this serves as a deflegmator. The condenser is a glass tube about 6 feet long, with two 30-inch glass water jackets mounted tandem. The condenser is connected tightly with the receiver, and from the latter a tube leads to the open air to carry off vapors that will not condense. The still rests upon (or in) another lemon-oil can from which the whole top has been cut away, while steam, generated in another room, is led through the partition and into the lower can. Usually 5 gallons of the crude gasoline are fractionated in a series of distillations: those fractions that will not serve for essential oil work are used in Roesse-Gottlieb determinations, etc.

#### VARIATIONS IN GASOLINE.

No one who has had occasion to study the behavior of “gasoline” during the past few years will be surprised at the statement that distillates boiling between 40° and 65° C. and derived from different lots of crude material have been found to vary somewhat in their behavior as solvents. In the case of the lot prepared for the assays discussed in the paper of 1914, it was found that the volume of oil (expressed in terms of the bottle graduation) obtained from 10 cc. of extract, when multiplied by 2, gave the true percentage of the oil in the extract. Similarly, if 5 cc. of extract had been used, the volume found was to be multiplied by 4. Of course, if 20 cc. of extract had been used, the volume found, in terms of bottle graduation, would equal the percentage

of oil in the extract; experience showed, however, that where more than 10 cc. of extract was employed, the calcium chloride solution would not, as a rule, cause the precipitation of all the oil present.

In the case of the 40-65° C. distillates prepared in recent years, it has sometimes been found that the even factors 2 and 4 did not serve to give the true percentage of oil present: in other words, the assumption that the volume of the gasoline-oil solution was exactly equal to the sum of the volume of the gasoline and that of the oil, did not hold. Apparently a slight contraction took place, and hence the difference between the volume of gasoline and that of the gasoline-oil solution had to be multiplied by a factor somewhat greater than 2 or 4, as the case might be, to yield the correct percentage. Once this factor has been determined for a given gasoline, it appears to hold in the case of any essential oil solution assayed. Thus, with the lot of gasoline recently prepared and employed in the determinations discussed later in this paper, the factors 2.1 and 4.2 were established with the aid of a standard solution of camphor (5 per cent). When 10 cc. portions of this solution were assayed, the average volume of camphor obtained was 2.38, in terms of Babcock bottle graduation:  $2.38 \times 2.1 = 4.998$  per cent. If the assay of a sample of camphor solution of unknown strength were to yield a volume of 2.30, under the same conditions, its content of camphor would then be  $2.30 \times 2.1 = 4.83$  per cent.

It goes without saying that when a high degree of accuracy is called for, care must be taken that the readings of the gasoline and gasoline solution columns shall be made at the same temperature. If a "blank" (a determination in which alcohol and gasoline alone are used with the calcium chloride solution) is run along with the oil determinations and the volume of gasoline thus found is deducted from the volume of the gasoline-oil solution, error because of possible temperature differences may be avoided.

The writer knows of a number of cases in which this method has been applied by other workers to the assay of alcoholic solutions of essential oils and of camphor, with but scant success. In some of these cases it has been found that no proper effort had been made to secure either accurately graduated apparatus or a suitable gasoline; in the other cases no information was obtained other than that satisfactory results were not secured. Believing that the method is one worthy of confidence, it has been thought well to call attention in this way to certain essential matters of technique and therefore to restate what is apparently the best procedure.

*Method for the Determination of Essential Oils in Certain Flavoring Extracts, and of Camphor and Peppermint Oil in Certain Pharmaceutical Preparations.*

**REAGENTS AND APPARATUS.**

(1) *Calcium chloride solution.*—In water mixed with about 4 per cent of its volume of concentrated hydrochloric acid, dissolve calcium chloride until a density of about 1.30 is obtained. Allow this solution to stand overnight and then filter perfectly clear. A large bottle provided with a siphon, at the end of which is a tap with a drawn-out tip, forms a convenient container for this solution.

(2) *Redistilled light gasoline.*—Fraction boiling between 40° and 65° C.

(3) *Milk-test bottles, 8 per cent, calibrated.*—If accurately graduated, the necks of these bottles will contain exactly 0.2 cc. between graduations indicating 1%.

(4) *Accurate full pipets.*—10 cc.; 5 cc.; 1 cc.; 0.5 cc. The 1 cc. and 0.5 cc. pipets are preferably made of thick-walled glass tubing of 2-3 mm. bore, drawn out to a long tip, which is bent slightly and filed flat at the end so as to deliver gasoline smoothly against the inner wall of the Babcock bottle's neck.

**DETERMINATION.**

(A) *For extracts containing approximately 5% of oil, e. g., orange extract and lemon extract; also for extracts containing approximately 3% of oil, e. g., peppermint extract and anise extract.*—Pipet 10 cc. of the extract into a carefully cleansed Babcock bottle; run in calcium chloride solution until the bottle is filled to the shoulder; shake to secure thorough mixing. Next run in *exactly* 1 cc. of gasoline—being careful that the tip of the gasoline pipet does not touch a wet spot on the neck of the bottle—and stopper the bottle tightly with a soft cork which has been wetted with the calcium chloride solution before insertion. Shake the bottle and its contents violently for a minute or two and centrifuge at fairly high speed for 2 minutes. Remove the stopper, add quickly calcium chloride solution until the whole gasoline column is within the graduated part of the bottle neck, recork, reverse the bottle so that the gasoline solution rises into the bulb and, while in this position, once more shake the bottle violently. Centrifuge at high speed for 3-5 minutes. Remove the bottle to a table before a window—being careful to keep it upright—and, with the aid of a magnifying glass, read off the exact length of the gasoline column in terms of the bottle graduation. The lower meniscus should be flat and sharply defined; if any whitish "collar" appears, it is probably due to lack of sufficient acid in the calcium chloride solution. The extreme upper and lower limits of the upper meniscus should be read and their mean taken as the upper reading.

A parallel determination in which 10 cc. of alcohol is used instead of the extract serves to measure the volume of gasoline delivered by the pipet, in terms of the bottle graduation. Deduct this volume from that of the gasoline-oil solution, and the difference thus obtained, multiplied by 2, gives the percentage of oil in the extract.

(B) *For extracts containing 7-15% of camphor or of essential oil, e. g., spirit of camphor U. S. P., or essence of peppermint U. S. P.*—Use 5 cc. of extract instead of 10 cc., and proceed as under (A). Calculate the percentage by multiplying by 4, instead of by 2, the difference between the reading found for the extract and that found for the blank.

(C) *For extracts containing as little as 2% of essential oil, e. g., nutmeg extract.*—Use not more than 0.5 cc. of gasoline to 10 cc. of extract; in other words, the gasoline volume should not be more than three times as great as the volume of the oil to be determined.

NOTE.—It is sometimes found that difficulties arise, due to the composition of the gasoline employed. It goes without saying that "gasoline" which boils above 40° and

below 65° C., is not always one and the same thing. To meet this difficulty, the following may be resorted to, supposing an orange extract of unknown composition is under examination: Determine the oil in a standard 5% orange extract and note whether 2, or 1.98, or 2.02, etc., is the factor to be used in calculating percentage from volume measured. Apply the same factor in the case of the unknown.

#### COMPARISON WITH FORMER WORK.

In the article published in 1914, it was set forth that satisfactory determinations of the oil present could not be made by this method in the case of the standard wintergreen, cloves, and cassia extracts. Cassia oil is almost insoluble in gasoline; in the case of wintergreen extract only about 80–90 per cent of the oil was apparently recovered; in the case of cloves extract, only about 70 per cent. Recently these experiments were carefully repeated, with the following results:

Cloves extract (2%): 10 cc. of extract used. Found: 1.44%; 1.46%; 1.51%; 1.60%; 1.52%; 1.52% when 0.4 cc. of gasoline was used.

Wintergreen extract (3%): 10 cc. of extract used. Found: 2.60%; 2.61% when 1 cc. of gasoline was used. Found: 2.89%; 2.86% when 0.4 cc. gasoline was used.

It should be noted, in passing, that better results were obtained in the case of the wintergreen extract when the volume of gasoline employed was only slightly greater than that of the oil to be determined: under these conditions the assay yielded results which averaged 2.875 per cent instead of 3 per cent. Where the volume of gasoline was more than three times as great as that of the oil to be determined, the error was three times as great.

Attempts to determine bitter almond oil in almond extract (1 per cent) were unsuccessful: the acidified calcium chloride solution apparently failed to set free any oil from the alcoholic solution.

The method was applied to a series of alcoholic solutions of rosemary, sweet basil, and sweet marjoram oils, not only to see whether it is applicable at all to these extracts, but to gain an idea of how great accuracy could be secured in the case of dilute solutions when care is taken to avoid known sources of error. All determinations made are here recorded, whether regarded as satisfactory or not.

(1) Rosemary extract (2%): 10 cc. used with 0.4 cc. of gasoline. Found: 2.00%; 1.90%; 1.96%; 1.90%.

(2) Rosemary extract (4%): 10 cc. used with 1 cc. of gasoline. Found: 3.97%; 4.02%.

(3) Rosemary extract (4%): 10 cc. used with 0.4 cc. of gasoline. Found: 4.29%.

(4) Basil extract (1%): 10 cc. used with 0.4 cc. of gasoline. Found: 0.50%; 0.63%; 0.77%.

(5) Basil extract (1%): 10 cc. used with 0.16 cc. of gasoline. Found: 1.10%; 1.05%.

(6) Basil extract (1%): 15 cc. used with 0.16 cc. of gasoline. Found: 0.73%; 0.69%.

(7) Marjoram extract (1%): 10 cc. used with 0.4 cc. of gasoline. Found: 0.65%; 0.49%; 0.46%.

(8) Marjoram extract (1%): 10 cc. used with 0.16 cc. of gasoline. Found: 0.91%; 0.96%.

In studying these results, one must bear in mind that in (1) 0.2 cc. of oil; in (2) and (3) 0.4 cc. of oil; in (4), (5), (7), (8), 0.1 cc. of oil; and in (6) 0.15 cc. of oil is to be set free, extracted, and *measured*. Also, that the volume of gasoline to be pipetted and measured ranges from 1 cc. down to only 0.16 cc.

The ratio, gasoline:oil is in (1) 2:1; in (2) 2.5:1; in (3) 1:1; in (4) and (7) 4:1; and in (5), (6), and (8) 1.6:1. It will be noted that (4) and (7) are the worst results—too much gasoline! Apparently, in (3) too little gasoline was used, but too much emphasis can not be placed on a single determination. In the case of (6) it was noted that the turbidity produced on mixing extract and calcium chloride solution was much less than in (4) and (5): the oil was only partially precipitated. Whereas, in this case, the ratio, calcium chloride solution:extract is about 35 cc.: 15 cc., in all the other cases it is about 40 cc.: 10 cc. Similar results were obtained ten years ago when an effort was made to secure more accurate assays through the use of more than 10 cc. of certain weak peppermint extracts: the precipitation of the oil was not complete.

The conditions probably vary with the several oils, but the following general deductions appear to be justified:

(1) At least four volumes of calcium chloride solution must be mixed with one volume of extract to secure complete precipitation.

(2) Apparently, satisfactory results can be secured, at least in the case of very weak extracts, only when the volume of gasoline used is somewhat greater than, but not more than three times as great as, the volume of the oil it is to extract.

Finally, in cases where only minute volumes of oil and gasoline are involved, thorough shaking and prolonged centrifuging at fairly high speed are necessary.

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